DERWENT-ACC-NO: 1993-364327
DERWENT-WEEK: 199346

TITLE: Antibacterial resin mouldings useful for contact lens and related containers - contain an antibacterial metal complex based on e.g. silver, copper, zinc, germanium etc.

PATENT-ASSIGNEE: SEIKO EPSON CORP[SHIH]

PRIORITY-DATA: 1992JP-0011857 (January 27, 1992) , 1991JP-0243643 (September 24, 1991) , 1991JP-0243644 (September 24, 1991) , 1991JP-0345345 (December 26, 1991) , 1992JP-0011856 (January 27, 1992)

PATENT-FAMILY:

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APPLICATION-DATA:

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INT-CL (IPC): A61L002/16; G02C007/04

ABSTRACTED-PUB-NO: JP 05269181A

BASIC-ABSTRACT: Moulding contains an antibacterial metal complex. Another new moulding has a chemically bonded antibacterial metal complex. Another moulding has a chemically bonded antibacterial organic cpd. The mouldings are pref. a contact lens or a container for storing the lenses, lens-storing agents, lens cleaners or solns. for storing, cleaning and disinfecting the lenses.

In a new prepn. of the moulding, one or more antibacterial

metals of Ag, Cu,
Zn, Ge, Sn, Bi and Co are mixed with a resin as acetonato complexes. In
another new prepn. of the moulding, functional gp. having a radical-polymerisable unsatd. double bond is bonded to the acetonato complex
of the metal and copolymerised with a polymerisable monomer to bond an
antibacterial complex to the resin.

USE/ADVANTAGE - The contact lenses and related containers control thoroughly
growth of bacteria and fungi over a long period, requires no disinfection and
causes little leaching out of antibacterial substances.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS:
ANTIBACTERIAL RESIN MOULD USEFUL CONTACT LENS RELATED CONTAINER CONTAIN
ANTIBACTERIAL METAL COMPLEX BASED SILVER COPPER ZINC GERMANIUM

DERWENT-CLASS: A96 D22 P34 P81

CPI-CODES: A04-A; A08-M02; A09-A; A12-L03; A12-P06; A12-V02A; D09-A01C;

ENHANCED-POLYMER-INDEXING:
Polymer Index [1.1]
017 ; P0000 ; S9999 S1434
Polymer Index [1.2]
017 ; ND01 ; ND04 ; B9999 B4513 B4466 ; Q9999 Q8297 Q8286 Q8264
; Q9999 Q8399*R Q8366
Polymer Index [1.3]
017 ; D61*R Ag 1B Tr Cu Zn 2B Bi 5A Sn 4A Ge Co 8B ; A999 A044*R
Polymer Index [2.1]
017 ; G0806 G0022 D01 D51 D53 F23 Ge 4A Sn Bi 5A Co 8B Tr Cu 1B
Ag Zn 2B ; H0011*R
Polymer Index [2.2]
017 ; ND01 ; ND04 ; B9999 B4513 B4466 ; Q9999 Q8297 Q8286 Q8264
; Q9999 Q8399*R Q8366

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0029
0105
0107
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Multipunch Codes: 017
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(71)Applicant : **SEIKO EPSON CORP**
(72)Inventor : **USHIYAMA YOICHI**
KATAGIRI KANJI
MIYABAYASHI TOSHIYUKI
KOJIMA TADAO
MOGAMI TAKAO

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(54) ANTIMICROBIAL RESIN MOLDING AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To obtain contact lenses, containers for preserving the contact lenses, containers for contact lens preservatives, containers for contact lens cleaners, or containers for dissolving water for the contact lens preservatives, cleaners and disinfectants which do not substantially generate bacteria, fungi, etc., do not require a sterilization treatment and substantially obviate the elution of antimicrobial materials.
CONSTITUTION: The antimicrobial org. materials are bonded by a copolymn., graft polymn. and other methods on the inside or surfaces of the contact lenses or the containers for the articles associated with the contact lenses or antimicrobial metals are securely bonded as complex thereto. The contact lenses and the containers for the articles associated with the contact lenses with which the generation of the bacteria, fungi, etc., is substantially prevented by the sterilization effect of the above-mentioned materials and which do not require the sterilization treatment are thereby obtd.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The antibacterial resin Plastic solid characterized by making an antibacterial metal complex intermingled.
[Claim 2] The antibacterial resin Plastic solid characterized by carrying out the chemical bond of the antibacterial metal complex.
[Claim 3] The antibacterial resin Plastic solid characterized by carrying out the chemical bond of the antibacterial organic compound.
[Claim 4] The antibacterial resin Plastic solid according to claim 1 characterized by being one sort or two sorts or more of the metals or metal ions which were chosen from the group which the metal or metal ion which has antibacterial [of the antibacterial metal complex made intermingled] becomes from silver, copper, zinc, germanium, tin, a bismuth, and cobalt.
[Claim 5] The antibacterial resin Plastic solid according to claim 2 characterized by being one sort or two sorts or more of the metals or metal ions which were chosen from the group which the metal or metal ion which has antibacterial [of the antibacterial metal complex which carries out a chemical bond] becomes from silver, copper, zinc, germanium, tin, a bismuth, and cobalt.
[Claim 6] The antibacterial resin Plastic solid according to claim 3 characterized by being one sort or two sorts or more of antibacterial organic compounds chosen from the group which an antibacterial organic compound becomes from chitosan or its derivative, chlorhexidine or its derivative, the benzalkonium chloride that is quarternary ammonium salt, benzethonium chloride or its derivative, an acridine, or its derivative.
[Claim 7] The antibacterial resin Plastic solid characterized by a resin Plastic solid according to claim 1 to 6 being a contact lens.
[Claim 8] The antibacterial resin Plastic solid characterized by a resin Plastic solid according to claim 1 to 6 being a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants.
[Claim 9] The manufacture method of the antibacterial resin Plastic solid characterized by making it intermingled in a resin by making into an acetonate complex one sort or two sorts or more of antibacterial metals chosen from the group which consists of silver, copper, zinc, germanium, tin, a bismuth, and cobalt.
[Claim 10] The manufacture method of the antibacterial resin Plastic solid characterized by combining the functional group which has the unsaturation double bond in which a radical polymerization is possible in an acetonate complex for one sort or two sorts or more of antibacterial metals chosen from the group which consists of silver, copper, zinc, germanium, tin, a bismuth, and cobalt, and combining an antibacterial organic compound with a resin by carrying out copolymerization of it to a polymerization nature monomer.
[Claim 11] The manufacture method of the antibacterial resin Plastic solid characterized by combining the functional group which has the unsaturation double bond in which a radical polymerization is possible with one sort or two sorts or more of antibacterial organic compounds chosen from the group which consists of chitosan or its derivative, chlorhexidine or its derivative, the benzalkonium chloride that is quarternary ammonium salt, benzethonium chloride or its derivative, an acridine, or its derivative, and combining an antibacterial organic compound with a resin by carrying out copolymerization of it to a polymerization nature monomer.
[Claim 12] The manufacture method of the antibacterial resin Plastic solid characterized by combining an antibacterial organic compound with a resin by making the hydroxyl group which one sort or two sorts or more of antibacterial organic compounds chosen from the group which consists of chitosan or its derivative, chlorhexidine or its derivative, the benzalkonium chloride that is quarternary ammonium salt, benzethonium chloride or its derivative, an acridine, or its derivative have react with the carboxyl group of a contact lens material, and building ether linkage.
[Claim 13] The manufacture method of the antibacterial resin Plastic solid characterized by combining an antibacterial organic compound with a resin by making the carboxyl group which one sort or two sorts or more of antibacterial organic compounds chosen from the group which consists of chitosan or its derivative, chlorhexidine or its derivative, the benzalkonium chloride that is quarternary ammonium salt, benzethonium chloride or its derivative, an acridine, or its derivative have react with the hydroxyl group of a contact lens material, and building ether linkage.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] If bacteria, mold, etc. say further about the resin Plastic solid which has antibacterial [which it hardly generates], and its manufacture method, this invention has antibacterial [which bacteria, mold, etc. hardly generate], namely, relates to safety and the easy contact lens of handling, a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container, dissolution water contact lens preservatives, cleaning agents and the containers for disinfectants, and those manufacture methods.
[0002]
[Description of the Prior Art] The contact lens generally used now is divided roughly into a hard lens and a soft contact lens. Each aforementioned contact lens has the advantage and demerit, respectively. That is, the hard lens has many advantages -- an eyesight straightening effect is excellent. On the other hand, it is easy to attach a blemish to a cornea mechanically, therefore obstacles, such as cornea infection, may be received. On the other hand, the feeling of wearing of a soft contact lens improves by leaps and bounds by hydrophilic grant, and shortage of supply of the oxygen to the cornea which was a problem until now is also being solved by water. However, as a result of the thing of water nature tending to receive contamination by the bacillus and continuing wearing to it and not knowing, infection, such as keratitis and a cornea ulcer, is often caused. Moreover, the sterilization processing for preventing it is very complicated, and has become the cause by which a soft contact lens is one with the low rate of wearing in the country compared with a hard lens.
[0003] Moreover, breeding of these microorganisms is suppressed by the bacteria and mold which were mixed into the container at the time of use also about the container of the related supply of a contact lens, i.e., a contact lens preservation container, the contact lens preservative container, the contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants breeding, starting secondary infection, and adding an antimicrobial agent into a preservative, a cleaning agent, etc. However, in order for it to be a contact lens to use a lot of antimicrobial agents or a strong antimicrobial agent, it has groped for the method of suppressing breeding of a microorganism, without adding an antimicrobial agent preferably also because of a cornea. Although development of the resin which covered the antibacterial substance is tried, it has much elution of an antimicrobial, and it is not suitable for a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants.
[0004]
[Problem(s) to be Solved by the Invention] Although it is said that a hard lens generally cannot receive contamination by the bacillus comparatively easily, it is infected with bacteria or mold during wearing, therefore a cornea may receive obstacles, such as infection. Since the material itself was a hydrophilic property, while a soft contact lens tended to cause the critical infection by breeding of bacteria, mold, etc. inside the lens and needed cautions for handling, sterilization and its sterilization operation were complicated.
[0005] Therefore, although the requests to the contact lens which has antibacterial were mounting, the technology which can meet the expectation was not developed before. For example, although the contact lens in which the resin coat containing a contact lens (JP,63-217319,A) and a chitosan derivative using the chitosan derivative as a base material was formed is proposed (JP,3-102313,A), the durability (life) of optical-character ability and antimicrobial activity is inadequate.
[0006] this invention is made in order to solve the above troubles. That is, the place made into the purpose of this invention has contamination by microorganisms, such as bacteria and mold, in offering the contact lens which hardly happens.
[0007]
[Means for Solving the Problem] It is characterized by the contact lens of this invention, a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants endowing antibacterial with a resin Plastic solid for an antibacterial metal complex or an antibacterial organic compound a chemical bond or by making it intermingled. Therefore, the power conditions which an antibacterial substance fulfills are as follows. (1) Since a contact lens touches a direct cornea and a conjunctiva upwards and the effluent from a lens shifts to an alimentary canal with tear fluid, it is necessary to pay attention to especially safety. Therefore, the antibacterial substance combined with a contact lens and the container relevant to it has high safety, (2) It differs from the functional group to which it has that antimicrobial activity is not lost by combination and the reaction machine which for that participates in combination with a lens, and the reaction machine discovers an antibacterial action, (3)

The optical-character ability which an original lens has when it combines with a lens material is not lost, Namely, compatibility with a lens monomer is good and the degree of option of a polymerization method is large, (4) -- not losing the processability which an original lens has when it combines with a lens material, and (5) -- they combine with a contact lens firmly, or it becomes a requirement that it is supplemented and there is almost no elution

[0008] In order that this invention persons may solve a technical problem, as a result of repeating research wholeheartedly, the method of combining a benzalkonium chloride, benzethonium chloride, etc. with a resin firmly also in the complex of an antibacterial metal, chitosan and its derivative, a biguanide derivative especially chlorhexidine, an acridine and its derivative, or in an ETAKU lysine and quarternary ammonium salt, with the above-mentioned conditions fulfilled is found out, and it came to complete this invention. the joint method to the above-mentioned antibacterial substances and those contact lenses is attached [it is alike and] and explained below

[0009] (1) From the antibacterial metal complex former, it is known that a certain kind of a metal or a metal ion has antibacterial or sterilization nature. For example, the silver nitrate is used as a disinfectant for some time. Antibacterial [of metals, such as silver, copper, lead, tin, zinc, a bismuth, cadmium, chromium, germanium, and cobalt, and those compounds] and sterilization nature are known similarly. It becomes an indispensable condition that the antibacterial substance combined with a contact lens and the container relevant to it has high safety and that combination is firm and there is almost no elution as stated previously. It is known that lead, cadmium, and chromium at least will have a bad influence on a living body from such a standpoint, and it is not desirable as an antibacterial substance combined with a contact lens and its related container. Silver, copper, tin, zinc, a bismuth, germanium, and cobalt are satisfactory if elution is a minute amount. It is known that germanium has a health operation (JP,63-25618,B), and a germanium joint resin can also be used for the purpose on health.

[0010] A large number [the method of combining or holding a metal or its ion]. For example, adhesion or content (JP,62-241939,A, JP,1-186804,A) of one zeolite

2) Mixing, covering (JP,63-25618,B)

3) Aluminosilicate (JP,2-46620,B)

4) N-long-chain acylamino silicate (JP,3-20363,A)

5) Hydroxyapatite (JP,3-90007,A)

** is reported. However, hydroxyapatite and an aluminosilicate do not have enough optical-character ability to use for a contact lens. or [moreover, / having joined together firmly since combination is weak and elution of an antibacterial metal takes place during wearing in mixing and covering of metal confidence] -- or being supplemented firmly is desirable

[0011] In order that this invention persons may solve a technical problem, as a result of repeating research wholeheartedly, the acetylacetonate metal complex which is the acetylacetone complex salt of an antibacterial metal, or the benzoyl acetonate metal complex which is benzoylacetone complex salt dissolved in many polymerization nature monomers which form transparent plastics suitable as a contact lens material, and found out being firmly incorporated into a polymerization constituent.

[0012] Since an antimicrobial copolymerized with the polymerization nature monomer of contact lens material and was directly incorporated into a polymer principal chain by adding the functional group which has the unsaturation double bond in which a radical polymerization is possible to the benzene ring of a benzoyl acetonate metal complex as a result of advancing research furthermore, it found out not being eluted at all by prolonged use. And are fully, and it is checked that the degree of option of a polymerization nature monomer and a polymerization method is also large, and the solubility over a polymerization nature monomer came to complete this invention.

[0013] (2) Antibacterial [of chitosan, and the derivative (a) chitosan and its derivative]: Chitosan checks growth of a detrimental microorganism like Escherichia coli also in a chitin derivative, respectively. Growth of a fusarium bacillus is completely prevented by the culture medium by chitosan addition 0.1%, and multiplication of Escherichia coli is prevented by chitosan concentration 0.02% (the Japan Society for Bioscience, Biotechnology and Agrochemistry western-part-of-Japan branch convention in the Showa 60 fiscal year, November 12, 1985, page 33 of a summary). The chitosan concentration which checks multiplication of these mold or bacteria changes with kinds of microorganism. Moreover, low-molecular chitosan prevents multiplication of these microorganisms by concentration lower than macromolecule chitosan. Moreover, it is reported that the polysaccharide which replaced the hydrogen of a hydroxyl group by the compound containing the 4th class ammonium also shows antibacterial (JP,3-70701,A).

[0014] (b) Combination to the contact lens of a chitosan derivative: There are various methods in combination to the synthetic macromolecule of a chitin derivative. For example, the method (1303 collection of the Society of Polymer Science, Japan lecture summaries : 39 (4) 1990) of turning carboxylation and the chitin derivative the diethylaminoethyl (it omitting Following DEAE) in the macromolecule front face, and combining both, respectively, is reported. Moreover, there is a method (JP,2-41473,A) of combining a chitin, chitosan, and its derivative with the hydroxyl group or carboxyl group of a high molecular compound using the poly isocyanate compound. In addition, a chitosan derivative is dissolved in a polar organic solvent, and the method (JP,63-217319,B) of making it process and construct a bridge by formaldehyde, the glutaraldehyde, or epichlorohydrin etc. is reported after fabrication. In order that this invention persons may solve a technical problem, as a result of repeating research wholeheartedly by considering the above-mentioned reaction as reference, it combined with the contact lens material, without chitosan or its derivative losing an original function, and the conditions which moreover discover antimicrobial activity are found out and it came to complete invention.

[0015] (3) Chlorhexidine is the most powerful germicide in the BISUJI guanide (bisdiguanide) compound studied by Davis (Davis, G.E.) of 1954 Britain and an I.C.I. lab, and being used as a disinfectant in clinical each field is reported to the British

pharmacology society magazine (British J.of Pharmacology, 9 , 192 (1954)). Although an antibacterial action is widely expressed to a Gram positive and a gram negative, it is more more effective than a gram negative to a gram positive. To the thing of Pseudomonas aeruginosa (Psudomonas) or Proteus (Proteus) of a certain kind, effect is comparatively weak, and it is invalid with an anti-acid bacillus, a spore, and a virus. in A vitro examination shows the sterilization effect stronger than other germicides, such as the fourth class ammonium system, a phenol system, or an iodine tablet. Effect will be reduced, if it is the strongest at neutral delicate alkalinity and the organic substance of blood and pus, and others exists. There are not penicillin sulfa drugs etc. and antagonism nature, and stimulative is weak and cannot produce resistant bacteria easily.

[0016] Combination to the contact lens of chlorhexidine: There are various methods in combination to the synthetic macromolecule of chlorhexidine. For example, various material is processed by the vinyl monomer which has an acidic group, and the copolymerized resin as given in JP,56-34203,B, after making the resin which has an acidic group adhere to various material-list sides, make the solution of a chlorhexidine salt contact, and it is made to react to the acidic group in the resin which contains chlorhexidine as a polymerization component, and fixes, and the method of endowing antibacterial with various material is learned.

[0017] Chlorhexidine or its salt this invention persons as a polymerization nature vinyl monomer Glycidyl methacrylate, A monomer, an acrylic acid with carboxyl groups, such as glycidyl acrylate A monomer, a styrene sulfonic acid with carboxyl groups, such as a methacrylic acid and an itaconic acid A monomer with sulfonic groups, such as a 2-acrylamide-isobutane sulfonic acid Acid anhydrides, such as a monomer and a maleic anhydride with ester machines, such as methyl acrylate, ethyl acrylate, and ethyl methacrylate, and itaconic acid anhydride, etc. in addition, by copolymerizing with a contact lens material It found out that it could be used as a safe contact lens which has antibacterial, with the optical-character ability and the feeling of wearing held which an original contact lens has. in addition, the functional group which has the unsaturation double bond in which a radical polymerization is possible is combined -- making -- it -- a polymerization nature monomer and copolymerization -- or graft polymerization can also be carried out

[0018] (4) ETAKU lysine It is the sterilization disinfectant which mho gene NOSU (Morgenroth), SHUNAIZA and others (Schnizer) improved the acriflavine in 1919, and was made as reported to the Pharmacopoea of Japan. There are bacteriostasis and a germicidal action to various suppuration bacilli especially a streptococcus, the Welch bacillus, staphylococcus, Neisseria gonorrhoeae, etc. in Although the diluted solution of 1:120 and 000 is also effective to a streptococcus in vitro, 1:40,000 is the minimum useful density in the living body. A stimulus is not given to a body tissue but there is the feature with which an operation does not decrease by existence of blood serum ****** by ******. Although an action mechanism is not clear, it is widely used as a few sterilization disinfectant of a side effect the flume crack which is for becoming acridinium ion and checking a bacterial respiratory enzyme, and now. However, before, as for the method of combining an ETAKU lysine or its derivative with resins, such as a contact lens, firmly, without making antibacterial losing, there was no report.

[0019] Hereafter, detailed explanation of this invention is given. Although it is required to replace by the functional group which has the functional group of a resin and reactivity in combining an ETAKU lysine to a synthetic macromolecule in the ethoxy basis of an ETAKU lysine by not making antimicrobial activity lose, it is possible when the amino group which is an active group attaches or carries out the reaction post reduction of the protective group which chooses the conditions which do not receive ornamentation. Wagner's and others method (72 Wagner et al., J.Am.Chem.Soc., 3477 (1950)) is applied, the ethoxy basis of an ETAKU lysine is replaced by the hydroxyl group, it is made to react with the carboxyl group of a contact lens, and an ETAKU lysine can be combined with a contact lens by ester combination. Vogel et al. [moreover,] (Vogel et al.:J.Chem.Soc., 616 (1948)) -- ** -- an ETAKU lysine can be combined with a lens according to ether linkage by making it react with the hydroxyl group of the synthetic macromolecule which will replace the ethoxy basis of an ETAKU lysine by the halogen if a reaction is used, and replaced hydrogen, and dehydrating

[0020] GUREDI et al. [furthermore,] (Gredy et al.:Bull.Soc.Chim.France and 3 (5) --) 1093 (1936), HENION et al. (56 Hennion et al:J.Am.Chem.Soc., 1802 (1934)), RAROKKU et al. (Larock et al.:J.Am.Chem.Soc. and 106 (15) --) The functional group which has the unsaturation double bond in which a radical polymerization is possible instead of the ethyl group of an ETAKU lysine if the reaction of 4218 (1984) is used, For example, by adding the compound which the vinyl group, the allyl group, the acrylic machine, the methacrylic machine, etc. added, an antimicrobial copolymerizes with the polymerization nature monomer of contact lens material, and can incorporate directly into a polymer principal chain.

[0021] (5) quarternary ammonium salt -- since it is old, a benzalkonium chloride, benzethonium chloride, and an organic silicon system ammonium salt are compounds suitable as an antibacterial organic compound for antibacterial contact lenses also in the quarternary ammonium salt used as a safe disinfectant antibacterial **** with strong quarternary ammonium salt -- things are known for many years Especially, a benzalkonium chloride and benzethonium chloride are widely used as a powerful high antimicrobial agent of safety, and are used also for the disinfection at the time of a surgical operation besides being used for disinfection of a hand, a leg, and a blemish at ordinary homes. Reporting that DOMAKKU (Domagk) will have powerful sterilizing properties in the thing of quarternary ammonium salt of a certain kind in 1935, still more detailed research about many surface activity compounds was done in 1940, the electrified bacteria were adsorbed in the electrified reverse nature soap, the biomass front face was piled up, and Coon (Kuhn) reported to make biomass ****** denaturalize. Although the general formula of quarternary ammonium salt is in [C6H5CH2N(CH3) 2R]+Cl-D and is shown, it turns out that R has sterilizing properties with the strong thing of the alkyl group of C8H17-C18H37, and the outstanding detergency in inside, and this matter is widely used as a benzalkonium chloride.

[0022] On the other hand, low rinses (Rawlins) (J. 32 Am.Pharm.Assoc., 11 (1943)), and Jos Lynn and others (32 Joslyn et

al., J.Am.Pharm.Assoc., 49 (1943)) compounded the quaternary ammonium compound, the sterilizing properties were studied, and benzethonium chloride and the methylbenzethonium chloride reported that it was the most powerful. Now, it is widely used as an antimicrobial agent that benzethonium chloride is also safe and powerful. However, before, as for the method of combining quarternary ammonium salt with resins, such as a contact lens, firmly, without making antibacterial and optical-character ability losing, there was no report.

[0023] The example of the joint method to the synthetic macromolecule of quarternary ammonium salt is given. GUREDI's and others reaction (Gredy et al.:Bull.soc.chim.France and 3 (5) --) 1093 (1936), HENION's and others reaction (56 Hennion et al:J.Am.Chem.Soc., 1802 (1934)), or Buckman's and others method (70 Bachman and Hellman, J.Am.Chem.Soc., 1772 (1948)) By adding the compound which the functional group which has the unsaturation double bond in which a radical polymerization is possible, for example, a vinyl group, the allyl group, the acrylic machine, the methacrylic machine, etc. added to quarternary ammonium salt, if it uses An antimicrobial copolymerizes with the polymerization nature monomer of contact lens material, and can incorporate directly into a polymer principal chain. Moreover, if Minagawa's and others method (Minagawa machine : ******, 17,256 (1976)) is applied, organic silicon system quarternary ammonium salt is fixable to a resin.

[0024] The above-mentioned antibacterial substance is an indispensable component for giving antibacterial, and it is desirable to contain 0.1 to 20% of the weight. An antibacterial effect is small in it being less than 0.1 % of the weight, and since compatibility with a polymerization nature monomer falls, nebula and cloudy weather occur on the contact lens obtained by carrying out a polymerization and transparency is lost when 20 % of the weight is exceeded, it is not desirable.

[0025] The contact lens which the antibacterial substance which is not eluted at all combined is obtained by prolonged use by the above-mentioned method. And there is solubility of enough over a polymerization nature monomer, and it is large. [of the degree of option of a polymerization nature monomer and a polymerization method] In addition, a sulfamine system antibiotic, a polymyxin system antibiotic, and a macrolide can also be used as an antibacterial substance for antibacterial contact lenses by the same reason.

[0026] The polymerization nature monomer in this invention is a compound which is generally used and in which a radical polymerization is possible, and the compound which contains a vinyl group, an allyl group, an acrylic machine, or an methacrylic machine in [one or more] a molecule is shown. Specifically, allyl compounds, such as vinyl compounds, such as acrylic esters (meta), such as alkyl (meta) acrylate, alkyl-halide (meta) acrylate, siloxanyl alkyl (meta) acrylate, fluoro (meta) acrylate, hydroxyalkyl (meta) acrylate, polyethylene-glycol (meta) acrylate, an acrylic ester (meta) of polyhydric alcohol, and vinyl (meta) acrylate, a derivative of styrene, N-vinyl lactam, and a carboxylic-acid (multiple valued) vinyl, a carboxylic-acid (multiple valued) allyl compound, and allyl-compound carbonate, etc. are mentioned. Still more specifically For example, styrene and a methyl styrene, dimethyl styrene, Crawl styrene, dichloro styrene, bromine styrene, p-crawl methyl styrene, A divinylbenzene, an acrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, phenyl acrylate, phenoxy ethyl acrylate, Acrylic-acid tetrahydrofurfuryl, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-acryloyloxyethyl succinic acid, 2-acryloyloxyethyl phthalic acid, a methacrylic acid, methyl methacrylate, Ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, Isobornyl methacrylate, benzyl methacrylate, phenyl methacrylate, Dicyclopentanil methacrylate, dicyclopentenylmethacrylate, 2-methacryloiloxy-ethyl succinic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxy butyl methacrylate, Fumaric-acid, maleic-acid, itaconic-acids and those ester, acrylonitrile, methacrylonitrile, N, and N-dimethyl acrylamide, an N-vinyl-2-pyrrolidone, a maleic anhydride, N-substitution maleimide, etc. are mentioned.

[0027] In order to raise crosslinking density, furthermore, ethylene glycol diacrylate, Diethylene glycol diacrylate, triethylene glycol diacrylate, 1, 6-hexanediol diacrylate, ethylene glycol dimethacrylate, Diethylene-glycol dimethacrylate, triethylene-glycol dimethacrylate, Propylene-glycol dimethacrylate, trimethylolpropanetrimethacrylate, A pentaerythritol thoria chestnut rate, 1, 4-butanediol dimethacrylate, Polyfunctional monomer, such as 1, 6-hexanedioldimethacrylate, glycerol dimethacrylate, a divinylbenzene diallyl phthalate, and diethylene-glycol bisallyl carbonate, can also be used.

[0028] The amount of dissolutions of the antibacterial substance to these polymerization nature monomers is not uniform, and, in the case of a contact lens, it is necessary to determine the addition of an antibacterial substance suitably in the range which maintains transparency and discovers antibacterial ability. It is used independently and also these polymerization nature monomers can also be used combining two or more sorts. Moreover, into the mixture which consists of a polymerization nature monomer, complex salt, and a polymerization initiator, little addition of a heat stabilizing agent, an antioxidant, a stain, a coloring agent, the ultraviolet ray absorbent, etc. can also be carried out if needed.

[0029] The polymerization of this invention is performed by irradiation of activity energy lines, such as heating or ultraviolet rays, under existence of the usual polymerization initiator. As a concrete polymerization initiator, a radical polymerization initiator is desirable, for example, benzoyl peroxide, diisopropyl peroxi dicarbonate, t-butylperoxy2-ethylhexanoate, t-butylperoxy perpivalate, t-butyl PAOKISHIJI iso butyrate, t-butylperoxyisopropylcarbonate, lauroyl peroxide, an azobisisobutyronitril, azobis (2,4-dimethylvaleronitrile), etc. are used. Moreover, in irradiation of an activity energy line, a sensitizer is used if needed [, such as the benzoin ether, / photopolymerization initiators or if needed]. The amount of these initiators used has the desirable amount percent of 0.001 - duplexs to the monomer to be used.

[0030] In addition, the monomer of ******** of a contact lens material is combinable with the peroxide generation and the graft polymerization to front faces, such as a contact lens. This is a thing which gives UV irradiation, corona discharge, or low-temperature plasma electric discharge, and generates the front face of a contact lens and which carries out the graft polymerization of the monomer radically. There is the method of using a lens the plasma treatment back, introducing a contact

lens into equipment by using a monomer as a steam or a liquid as a method, by the glow discharge under reduced pressure of 10-3 - 10torr, taking out after the method of making it react that it is directly radical or low-temperature plasma treatment and a processed base material from equipment, and making it react with a monomer.
[0031] The method of combining the method of making the above-mentioned antibacterial metal complex intermingled in a resin and an antibacterial metal complex, or an antibacterial organic compound to a resin is widely [not only a contact lens, a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants but] applicable to manufacture of an antibacterial resin organizer. As examples other than the above, the plastic referring to the direct skins, such as accessories, such as baby goods, such as tableware, such as cooking supplies, such as a cutting board, and chopsticks made from plastics, and a teacup, and a toy, and a feeding bottle, and a pierced earring, and an automatic thermometer, and membrane, a bathtub, a toilet bowl, etc. mold, and the plastics material used in the place which bacteria tend to generate is mentioned.
[0032]
[Function] The resin Plastic solid, i.e., a contact lens, which combined the antibacterial metal complex or the antibacterial organic compound of this invention, a contact lens preservation container, a contact lens preservative container, a contact lens cleaning agent container or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants, and the above-mentioned resin Plastic solid that made the antibacterial metal complex intermingled are preventing generating of microorganisms, such as mold and bacteria. It is not necessary to improve safety, to omit complicated sterilization operation and to add an antimicrobial agent.
[0033]
[Example] Although an example explains in more detail below, this invention is not limited to these.
[0034] (Example 1)
1. When chloro styrene 13.8g and dryness ether 100ml were put into the synthetic flask of synthetic (1) zinc complex of an antibacterial metal complex and metal magnesium 2.4g was added to this, the reaction occurred with generation of heat. When the reaction was completed enough, acetonitrile 4.1g was added to this and it stirred at the room temperature for 10 hours. When water and a small amount of hydrochloric acid were added to reaction mixture, it understood an added water part and the vinyl phenyl methyl ketone was obtained. When vinyl phenyl-methyl-ketone 7.2g and 4.4g of ethyl acetate were dissolved in dryness ether 100ml, the sodium ethoxide was added to this as a catalyst and it flowed back at 50 degrees C, the condensation reaction was started and the vinyl benzoylacetone was obtained. Vinyl benzoylacetone 2.3g obtained by the above-mentioned method was dissolved in 100ml of aqueous ammonia solutions 5%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the zinc acetate solution which dissolved 1.4g of zinc acetate in 100ml water. When these settlings were washed and it dried, vinyl benzoyl acetonate zinc was obtained.
[0035] (2) The vinyl benzoylacetone was compounded by the same method as composition (1) of a copper complex.
The above-mentioned vinyl benzoylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 5%, and in addition, the settlings of a bluish green color were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the copper acetate solution which dissolved 1.4g of copper acetate in 100ml water. When these settlings were washed and it dried, vinyl benzoyl acetonate copper was obtained.
[0036] (3) The vinyl benzoylacetone was compounded by the same method as composition (1) of a silver complex.
Obtained vinyl benzoylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 15%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the silver-nitrate solution which dissolved 1g of silver nitrates in 10ml water. When these settlings were washed and it dried, vinyl benzoyl acetonate silver was obtained.
[0037] (4) The vinyl benzoylacetone was compounded by the same method as composition (1) of a germanium complex.
Obtained vinyl benzoylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 10%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the germanium-dioxide solution which dissolved 0.2g of germanium dioxides in 100ml water. When these settlings were washed and it dried, vinyl benzoyl acetonate germanium was obtained.
[0038] (5) The vinyl benzoylacetone was compounded by the same method as composition (1) of a tin complex.
Obtained vinyl benzoylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 5%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the tin-oxide solution which dissolved 1.4g of tin oxides in 100ml water. When these settlings were washed and it dried, vinyl benzoyl acetonate tin was obtained.
[0039] 2. a contact lens -- production (sample 1) -- two -- two -- three -- three -- four -- four -- four -- - -- heptafluoro -- butyl -- methacrylate -- 50 -- a weight -- the section -- MECHIRUJI (trimethylsiloxy) -- silyl -- a propyl -- methacrylate -- 48 -- a weight -- the section -- (-- one --) -- - -- (-- five --) -- having compounded -- a metal complex -- some -- one -- a sort -- one -- a weight -- the section -- ethylene glycol -- dimethacrylate -- 0.7 This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed.

The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.
[0040] (Sample 2) The methyl methacrylate 94.8 weight section, the triethylene-glycol dimethacrylate 4 weight section, the one-sort [any] 1 weight section of the metal complex compounded by (1) - (5), and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced.
[0041] (Sample 3) The 2-hydroxyethyl methacrylate 69.7 weight section, the methyl methacrylate 24.6 weight section, the ethylene glycol dimethacrylate 0.4 weight section, the one-sort [any] 5 weight section of the metal complex compounded by (1) - (5), and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
[0042] (Sample 4) 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, the one-sort [any] 1 weight section of the metal complex compounded by (1) - (5), and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
[0043] (Sample 5) The 2, 3-dihydroxy propyl methacrylate 69.95 weight section, methyl methacrylate 26 weight section, ethylene glycol dimethacrylate 1 weight section, one-sort [any] 3 weight section [of the metal complex compounded by (1) - (5)], 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide 0.05 weight section was often mixed, and deaeration of this mixture and the nitrogen purge were performed. It was dropped at the glass type which fabricated this mixture in the contact lens configuration, 80 W/cm high-pressure mercury lamp was used for this, and ultraviolet rays were irradiated for 100 seconds in 10cm of distance. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making the obtained contact lens swell in pure water and washing it.
[0044] 3. Number measuring method of evaluation bacilli of antimicrobial activity. All the following operations were performed in sterile.
cultivation of I and a bacillus: the following bacilli -- respectively -- a slant medium -- 37 degrees C and the 16 - 24-hour 3rd at least] generation passage -- carrying out -- 8-10ml of bouillon -- a transplant -- it cultivates for 16 to 24 hours, and let 37 degrees C be fungus liquid This bacillus was saved at 15 degrees C, and was used within three days.
RO, assay strain: Escherichia coli (Escherichia coli)
HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 103 to 3.0x104. It was immersed in the 1ml of the above-mentioned fungus liquid, and the sample which carried out ultraviolet-rays sterilization was saved at 37 degrees C. The culture medium 18 hours after after a preservation start was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0045] The result which evaluated the antimicrobial activity of the contact lens of the samples 1-5 produced combining respectively each antibacterial metal complex compounded by (1) - (5) by the method of the above 3 is shown in Table 1. Moreover, in front Naka, "contrast" shows the contact lens produced by the composition as each sample with other same composition except for the point which does not contain an antibacterial metal complex.
[0046] Moreover, although each sample was boiled and the existence of the elution matter was checked, elution of an antibacterial substance was checked from no sample.
[0047]
[Table 1]

	試料1	試料2	試料3	試料4	試料5
亜鉛錯体	6×10^{4}	10^{4}	$<10^{2}$	$<10^{2}$	$<10^{2}$
銅錯体	2×10^{3}	$<10^{2}$	$<10^{2}$	$<10^{2}$	$<10^{2}$
銀錯体	$<10^{2}$	$<10^{2}$	$<10^{2}$	$<10^{2}$	$<10^{2}$
ｹﾞﾙﾏﾆｳﾑ錯体	$>10^{8}$	$>10^{8}$	2×10^{4}	3×10^{4}	6×10^{4}
錫錯体	5×10^{4}	9×10^{3}	$<10^{2}$	$<10^{2}$	$<10^{2}$
対照	$>10^{8}$	$>10^{8}$	$>10^{8}$	$>10^{8}$	$>10^{8}$

[0048] (Example 2)
(1) The polymerization of a contact lens, cutting, polish: A room temperature is sufficient and the 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl methacrylate 51 weight section, the MECHIRUJI (trimethylsiloxy) silyl propyl methacrylate 48 weight section, the ethylene glycol dimethacrylate 0.7 weight section, and the isopropyl par carbonate 0.3 weight section were mixed. This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed. The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.
(2) Plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.
(3) Graft polymerization: The contact lens which carried out plasma treatment to 3ml of 10-% of the weight acetylacetone solutions of the vinyl benzoyl acetonate silver compounded by (3) of an example 1 by (2) was added, it sealed after deaeration quickly, and graft polymerization processing for 5 minutes was performed at 35 degrees C.
[0049] (Example 3)
(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 71.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained.
(2) Plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.
(3) Graft polymerization: The contact lens which carried out plasma treatment to 3ml of 10-% of the weight acetylacetone solutions of the vinyl benzoyl acetonate silver compounded by (3) of an example 1 by (2) was added, it sealed after deaeration quickly, and graft polymerization processing for 5 minutes was performed at 35 degrees C.
(4) Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
[0050] The result which evaluated the antimicrobial activity of the contact lens produced in the examples 2 and 3 by the method shown 3 of an example 1 is shown in Table 2. Moreover, in front Naka, "contrast" shows the contact lens before carrying out surface treatment by the same composition as each example. Moreover, although the contact lens of each example was boiled and the existence of the elution matter was checked, elution of an antibacterial substance was checked from no sample.
[0051]
[Table 2]

	実施例2	実施例3
銀錯体	8×10^{3}	2×10^{4}
対照	$>10^{8}$	$>10^{8}$

[0052] (Example 4)
(1) Composition of acetylacetonate silver: Acetylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 15%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the silver-nitrate solution which dissolved 1g of silver nitrates in 10ml water. Acetylacetonate silver was obtained, when these

settlings were washed and it dried.
(2) Production of a contact lens : the 2-hydroxyethyl methacrylate 69.7 weight section, the methyl methacrylate 24.6 weight section, the ethylene glycol dimethacrylate 0.4 weight section, the acetylacetonate silver 5 weight section compounded by (1), and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. The obtained rod was ground after cutting and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
[0053] (Example 5)
(1) Composition of benzoyl acetonate silver: Benzoylacetone 2.3g was dissolved in 100ml of aqueous ammonia solutions 15%, and in addition, white settlings were obtained gradually, stirring this vinyl benzoylacetone-aqueous ammonia solution in the silver-nitrate solution which dissolved 1g of silver nitrates in 10ml water. When these settlings were washed and it dried, benzoyl acetonate silver was obtained.
(2) Production of a contact lens: The 2-hydroxyethyl methacrylate 69.7 weight section, the methyl methacrylate 24.6 weight section, the ethylene glycol dimethacrylate 0.4 weight section, the benzoyl acetonate silver 5 weight section compounded by (1), and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. The obtained rod was ground after cutting and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
[0054] The result which evaluated the antimicrobial activity of the contact lens produced in the examples 4 and 5 by the method shown 3 of an example 1 is shown in Table 3. Moreover, in front Naka, "contrast" shows the contact lens produced by the composition as each example with other same composition except for the point which does not contain an antibacterial metal complex. Moreover, although the contact lens of each example was boiled and the existence of the elution matter was checked, elution of an antibacterial substance was checked from no sample.
[0055]
[Table 3]

	実施例4	実施例5
銀錯体	3×10^{5}	10^{6}
対照	$>10^{8}$	$>10^{8}$

[0056] (Example 6) Composition of (1) vinyl benzoyl acetonate silver: It compounded by the same method as (3) of an example 1.
(2) Polymerization of vinyl benzoyl acetonate silver: The methyl methacrylate 94.8 weight section, the acetylacetonate silver 5 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. The obtained rod was ground and antibacterial resin powder was produced.
(3) Production of an antibacterial contact lens container: It often mixed, injection molding of the antibacterial powder 10 weight section produced by the polyethylene 90 weight section and (2) was carried out, and the contact lens container was produced.
(4) Antibacterial measurement: The number measuring method of bacilli. All the following operations were performed in sterile.
I, cultivation of a bacillus: It carried out by the same method as an example 1.
[0057] RO, assay strain: Escherichia coli (Escherichia coli)
HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 103 to 3.0x104. (1) It prepared by - (2), the 1ml of the above-mentioned fungus liquid was put into the contact lens container which carried out ultraviolet-rays sterilization, and it saved at 37 degrees C. The culture medium 18 hours after after a preservation start was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0058] The result which evaluated the antimicrobial activity of the contact lens container produced by above-mentioned (1) -

(3) by the method of the above (4) is shown in Table 4. Moreover, in front Naka, "contrast" shows the contact lens container produced by the composition as each example with other same composition except for the point which does not contain an antibacterial metal complex. Moreover, although the above-mentioned contact lens container was boiled and the existence of the elution matter was checked, elution of the **** matter was not checked.

[0059]

[Table 4]

	実施例6
銀錯体	$<10^2$
対照	$>10^8$

[0060] (Example 7)

(1) The polymerization of a contact lens, cutting, polish : a room temperature is sufficient and the 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl methacrylate 50 weight section, the MECHIRUJI (trimethylsiloxy) silyl propyl methacrylate 49 weight section, the ethylene glycol dimethacrylate 0.7 weight section, and the isopropyl par carbonate 0.3 weight section were mixed. This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed. The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.

[0061] (2) Combination of the chitosan to a contact lens : 1 plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.

2) Graft polymerization: It flooded with the acrylic acid, 60 degrees C of contact lenses which carried out plasma treatment were warmed for 1 hour, and the lens front face was made to carry out the graft polymerization of the acrylic acid.

3) Combination of the chitosan to a contact lens: The contact lens which carried out the graft polymerization of the acrylic acid was made to immerse and react to carbodiimide solution. Next, the DEAE-chitin which diethylamino ethyl alcohol was made to react to a chitin under sulfuric-acid existence, and was compounded was added, and the chitin was fixed according to covalent bond. It deacetylated by the sodium hydroxide 40% after washing using 2M acetic-acid buffer solution (pH 4), and the contact lens which chitosan combined was obtained.

(3) Antibacterial measurement: All operations below the number measuring method of bacilli were performed in sterile. cultivation of I and a bacillus: the following bacilli -- respectively -- a slant medium -- 37 degrees C and the 16 - 24-hour 3rd at least] generation passage -- carrying out -- 8-10ml of bouillon -- a transplant -- it cultivates for 16 to 24 hours, and let 37 degrees C be fungus liquid This bacillus was saved at 15 degrees C, and was used within three days.

RO, assay strain: Escherichia coli (Escherichia coli) and Staphylococcus aureus (Staphylococcus aureus ATCC 6538P)

HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 5.0x105 to 3.0x106. (1) It prepared by - (2), and it was immersed in the 1ml of the above-mentioned fungus liquid, and the contact lens which carried out ultraviolet-rays sterilization was saved at 37 degrees C. The culture medium of after (after [a preservation start] 0 hour and, and 18 hours) was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).

[0062] (Example 8)

(1) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 95.7 weight section, the triethylene-glycol dimethacrylate 4 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced.

(2) Combination of the chitosan to a contact lens: The chitosan acetate solution was prepared 1% to the solution of an acetic acid 5%, and the contact lens produced in this was immersed. After drying this, chitosan was combined with the contact lens in the poly isocyanate and the polyethylene glycol.

(3) Antibacterial measurement: The same method as an example 7 was used.

[0063] (Example 9)

(1) The polymerization of a contact lens, cutting, polish: The 2-hydroxyethyl methacrylate 97.7 weight section, the ethylene glycol dimethacrylate 2 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube

was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(2) Combination of the chitosan to a contact lens: The produced contact lens was processed by the sodium hydroxide after being immersed in N-methyl pyrrolidone solution of chitosan, and the bridge was made to process and construct by the dimethylformamide.
(3) Antibacterial measurement: The same method as an example 7 was used.
[0064] (Example 10)
(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 71.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(2) Combination of the chitosan to a contact lens: The same method as an example 7 was used.
(3) Antibacterial measurement: The same method as an example 7 was used.
[0065] (Example 11)
(1) The polymerization of a contact lens, cutting, polish: The 2, 3-dihydroxy propyl methacrylate 69.95 weight section, methyl methacrylate 26 weight section, ethylene glycol dimethacrylate 1 weight section, tris benzoyl acetonate neodymium 3 weight section, 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide 0.05 weight section was often mixed, and deaeration of this mixture and the nitrogen purge were performed. It was dropped at the glass type which fabricated this mixture in the contact lens configuration, 80 W/cm high-pressure mercury lamp was used for this, and ultraviolet rays were irradiated for 100 seconds in 10cm of distance. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making the obtained contact lens swell in pure water and washing it.
(2) Combination of the chitosan to a contact lens: The same method as an example 7 was used.
(3) Antibacterial measurement: The same method as an example 17 was used.
[0066] The result of the antimicrobial activity in each example is shown below.
[0067]
[Table 5]

実施例	残存菌数	
番号	大腸菌	黄色ブドウ球菌
7	2.0×10^4	4.1×10^4
8	1.0×10^4	5.1×10^3
9	<20	<20
10	<20	<20
11	<20	<20

[0068] A result shows the number of residual bacilli 18 hours after preservation.
[0069] (Example 12)
(1) The polymerization of a contact lens, cutting, polish: A room temperature is sufficient and the 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl methacrylate 50 weight section, the MECHIRUJI (trimethylsiloxy) silyl propyl methacrylate 49 weight section, the ethylene glycol dimethacrylate 0.7 weight section, and the isopropyl par carbonate 0.3 weight section were mixed. This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed. The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.
(2) Combination of the chlorhexidine to a contact lens : 1 plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.
2) Graft polymerization: It was immersed in chlorhexidine solution, 60 degrees C of contact lenses which carried out plasma

treatment were warmed for 1 hour, and the lens front face was made to carry out the graft polymerization of the chlorhexidine.

[0070] (3) Antibacterial measurement: All operations below the number measuring method of bacilli were performed in sterile.
cultivation of I and a bacillus: the following bacilli -- respectively -- a slant medium -- 37 degrees C and the 16 - 24-hour 3rd at least] generation passage -- carrying out -- 8-10ml of bouillon -- a transplant -- it cultivates for 16 to 24 hours, and let 37 degrees C be fungus liquid This bacillus was saved at 15 degrees C, and was used within three days.
RO, assay strain: Escherichia coli (Escherichia coli) and Staphylococcus aureus (Staphylococcus aureus ATCC 6538P)
HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 5.0x105 to 3.0x106. (1) It prepared by - (2), and it was immersed in the 1ml of the above-mentioned fungus liquid, and the contact lens which carried out ultraviolet-rays sterilization was saved at 37 degrees C. The culture medium of after (after [a preservation start] 0 hour and, and 18 hours) was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0071] (Example 13)
(1) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 96 weight section, the triethylene-glycol dimethacrylate 4 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced.
(2) Combination of the chlorhexidine to a contact lens: The same method as an example 12 was used.
(3) Antibacterial measurement: The same method as an example 12 was used.
[0072] (Example 14)
(1) The polymerization of a contact lens, cutting, polish: The 2-hydroxyethyl methacrylate 96.7 weight section, the ethylene glycol dimethacrylate 2 weight section, the chlorhexidine 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(2) Antibacterial measurement: The same method as an example 12 was used.
[0073] (Example 15)
(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, the chlorhexidine 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(2) Antibacterial measurement: The same method as an example 12 was used.
[0074] (Example 16)
(1) The polymerization of a contact lens, cutting, polish: The 2, 3-dihydroxy propyl methacrylate 68.95 weight section, methyl methacrylate 26 weight section, ethylene glycol dimethacrylate 1 weight section, tris benzoyl acetonate neodymium 3 weight section, chlorhexidine 1 weight section, 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide 0.05 weight section was often mixed, and deaeration of this mixture and the nitrogen purge were performed. It was dropped at the glass type which fabricated this mixture in the contact lens configuration, 80 W/cm high-pressure mercury lamp was used for this, and ultraviolet rays were irradiated for 100 seconds in 10cm of distance. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making the obtained contact lens swell in pure water and washing it.
(2) Antibacterial measurement: The same method as an example 12 was used.
[0075] (Example 17)
(1) Composition of vinyl chlorhexidine: The dimethyl sulfate was made to act on chlorhexidine under sodium-amide existence, and vinyl chlorhexidine was compounded.
(2) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, the vinyl chlorhexidine 1 weight

section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 12 was used.
[0076] The result of the antimicrobial activity of each example is shown below. Moreover, in front Naka, "contrast" shows the contact lens which is not carrying out surface treatment in examples 12 and 13, and other composition shows the same contact lens as each example except for the point which does not contain an antibacterial substance in examples 14-17.
[0077]
[Table 6]

実施例	残存菌数	
番号	大腸菌	黄色ブドウ球菌
12	< 20	< 20
13	< 20	< 20
14	< 20	< 20
15	< 20	< 20
16	< 20	< 20
17	< 20	< 20
対照12	$> 10^8$	$> 10^8$
対照13	$> 10^8$	$> 10^8$
対照14	$> 10^8$	$> 10^8$
対照15	$> 10^8$	$> 10^8$
対照16	$> 10^8$	$> 10^8$
対照17	$> 10^8$	$> 10^8$

[0078] A result shows the number of residual bacilli 18 hours after preservation.
[0079] (Example 18)
(1) The polymerization of a contact lens, cutting, polish: A room temperature is sufficient and the 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl methacrylate 50 weight section, the MECHIRUJI (trimethylsiloxy) silyl propyl methacrylate 49 weight section, the ethylene glycol dimethacrylate 0.7 weight section, and the t-butyl-peroxy-neodecanate 0.3 weight section were mixed. This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed. The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.
(2) Combination of the ETAKU lysine to a contact lens : ** ethylation of 1 ETAKU lysine: Hydrogen iodide was made to act on an ETAKU lysine, and the ethoxy basis was replaced by the hydroxyl group.
2) Plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.
3) Combination of the ETAKU lysine to a contact lens: It was immersed in the ** ethyl ETAKU lysine, the 60 degrees C of the above-mentioned activation contact lenses were warmed for 1 hour, and the contact lens which the ETAKU lysine combined was obtained.
[0080] (3) Antibacterial evaluation: All operations below the number measuring method of bacilli were performed in sterile. cultivation of I and a bacillus: the following bacilli -- respectively -- a slant medium -- 37 degrees C and the 16 - 24-hour 3rd at least] generation passage -- carrying out -- 8-10ml of bouillon -- a transplant -- it cultivates for 16 to 24 hours, and let 37 degrees C be fungus liquid This bacillus was saved at 15 degrees C, and was used within three days.
RO, assay strain: Escherichia coli (Escherichia coli) and Staphylococcus aureus (Staphylococcus aureus ATCC 6538P)
HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 5.0x103 to 3.0x106. (1) It prepared by - (2), and it was immersed in the 1ml of the above-mentioned fungus liquid, and the contact lens which carried out ultraviolet-rays sterilization was saved at 37 degrees C. The culture medium of after (after [a preservation start] 0 hour and, and 18 hours) was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the

culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0081] (Example 19)
(1) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 96 weight section, the triethylene-glycol dimethacrylate 4 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced.
(2) Combination of the ETAKU lysine to a contact lens: Hydrogen iodide was made to act on an ETAKU lysine, and the ethoxy basis was replaced by the hydroxyl group. Next, the hydrogen bromide replaced the hydroxyl group with the bromine atom, and 2-hide ROKISHI -6 and 9-acridine diamine were obtained. On the other hand, metallic sodium was made to react to a contact lens base material, the hydrogen of a hydroxyl group was replaced by sodium, and the activated contact lens was obtained. Lens ** was combined according to ether linkage by making 2-hide ROKISHI -6 and 9-acridine diamine react with an activation contact lens. The contact lens which two amino groups which oxidized at the end were returned [contact lens] with the inside of a glacial acetic acid, the stannous chloride, and the hydrochloric acid, and combined the ETAKU lysine was obtained.
(3) Antibacterial evaluation: The same method as an example 18 was used.
[0082] (Example 20)
(1) 6 and 9-diamino-2-bitter taste RIJINOKISHI ethylene (2-BINIROKISHI -6, 9-acridine diamine) Composition: Make hydrogen iodide act on 1 ETAKU lysine, and it is 2-hydroxy. - It considered as 6 and 9-acridine diamine.
2) Make ethylene carbonate act on this and it is beta-hydroxyethyl. 6, 9-diamino-2-acridinyl It considered as the ether.
3) It dehydrated under sulfuric-acid existence and 6 and 9-diamino-2-bitter taste RIJINOKISHI ethylene was compounded.
(2) The polymerization of a contact lens, cutting, polish: The 2-hydroxyethyl methacrylate 97 weight section, the ethylene glycol dimethacrylate 2 weight section, and the ETAKU lysine 1 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 18 was used. However, sterilization used sterilization by high pressure steam.
[0083] (Example 21)
(1) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Composition: Make hydrogen iodide act on 1 ETAKU lysine, and it is 2-hydroxy. - It considered as 6 and 9-acridine diamine.
2) The dimethyl sulfate was made to act on this under sodium-amide existence, and 6 and 9-diamino-2-bitter taste RIJINOKISHI ethylene was compounded.
(2) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, 6, the 9-diamino-2-bitter taste RIJINOKISHI ethylene 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 28 was used.
[0084] (Example 22)
(1) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Composition: Make hydrogen iodide act on 1 ETAKU lysine, and it is 2-hydroxy. - It considered as 6 and 9-acridine diamine.
2) Acetylene gas was made to act on this and 6 and 9-diamino-2-bitter taste RIJINOKISHI ethylene was compounded.
(2) The polymerization of a contact lens, cutting, polish: The 2, 3-dihydroxy propyl methacrylate 68.95 weight section, methyl methacrylate 29 weight section, ethylene glycol dimethacrylate 1 weight section, 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene 1 weight section, 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide 0.05 weight section was often mixed, and deaeration of this mixture and the nitrogen purge were performed. It was dropped at the glass type which fabricated this mixture in the contact lens configuration, 80 W/cm high-pressure mercury lamp was used for this, and ultraviolet rays were irradiated for 100 seconds in 10cm of distance. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making the obtained contact

lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 30 was used.
[0085] (Example 23)
(1) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Composition: It carried out by the same method as an example 21.
(2) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 4 weight section, ethylene glycol dimethacrylate 1 weight section, 2-hydroxyethyl methacrylate 83.7 weight section, N, and N-dimethyl acrylamide 10 weight section, 6, the 9-diamino-2-bitter taste RIJINOKISHI ethylene 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 18 was used.
[0086] (Example 24)
(1) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Composition: It compounded by the same method as an example 21.
(2) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Polymerization: The methyl methacrylate 94.8 weight section, 6, the 9-diamino-2-bitter taste RIJINOKISHI ethylene 5 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the metal mold of a contact lens container, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. This metal mold was heated at 70 degrees C for 1 hour, it heated at 100 degrees C among the air furnace further for 1 hour, the polymerization was performed, and the contact lens container was obtained.
(3) Antibacterial measurement: The number measuring method of bacilli. All the following operations were performed in sterile.
I, cultivation of a bacillus: It carried out by the same method as an example 18.
RO, assay strain: Escherichia coli (Escherichia coli)
HA, antibacterial evaluation: Using the nutrient broth culture medium, the bacillus was prepared so that the number of bacilli per ml might be set to 103 to 3.0x104. (1) It prepared by - (2), the 1ml of the above-mentioned fungus liquid was put into the contact lens container which carried out ultraviolet-rays sterilization, and it saved at 37 degrees C. The culture medium 18 hours after after a preservation start was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0087] (Example 25)
(1) Composition of 6 and 9-diamino-2-bitter taste RIJINOKISHI ethylene : it carried out like the example 20.
(2) 6, 9-diamino-2-bitter taste RIJINOKISHI ethylene Polymerization: The methyl methacrylate 94.8 weight section, 6, the 9-diamino-2-bitter taste RIJINOKISHI ethylene 5 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. This sealed tube was heated at 70 degrees C among warm water for 1 hour, was further heated at 100 degrees C among the air furnace for 1 hour, the polymerization was performed, and the round bar was obtained. The obtained rod was ground and antibacterial resin powder was produced.
(3) Production of an antibacterial contact lens container: It often mixed, injection molding of the antibacterial powder 10 weight section produced by the polyethylene 90 weight section and (2) was carried out, and the contact lens container was produced.
(4) Antibacterial measurement: It carried out by the same method as an example 24.
[0088] (Example 18 of comparison)
(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 27 weight section, the ethylene glycol dimethacrylate 1 weight section, the ETAKU lysine 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial evaluation: The same method as an example 18 was used.
[0089] The result of the antimicrobial activity of each example and the example of comparison is shown below.
[0090]
[Table 7]

実施例 番号	残存菌数	
	大腸菌	黄色ブドウ球菌
18	≦20	＜20
19	≦20	20
20	≦20	≦20
21	≦20	≦20
22	≦20	≦20
23	＜20	＜20
比較例18	＞10^8	＞10^8

[0091]
[Table 8]

実施例 番号	残存菌数	
	大腸菌	黄色ブドウ球菌
24	≦ 20	≦ 20
25	≦ 20	≦ 20
対照24	≧ 10^8	≧ 10^8
対照25	≧ 10^8	≧ 10^8

[0092] A result shows the number of residual bacilli 18 hours after preservation. Moreover, the contrast in examples 24-25 puts a contact lens container with the same other composition excluding an antibacterial substance. The contact lens and contact lens container which were shown in each example were boiled, respectively, and the existence of elution was checked. Elution of an antibacterial substance was checked [container / contact lens] from neither of the contact lenses. On the other hand, elution was accepted from the contact lens shown in the example of comparison.
[0093] (Example 26)
(1) The polymerization of a contact lens, cutting, polish : a room temperature is sufficient and the 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl methacrylate 50 weight section, the TORIMECHIRU [2-[triethoxy silyl] propyl] ammonium-salt 5 weight section, the MECHIRUJI (trimethylsiloxy) silyl propyl methacrylate 44 weight section, the ethylene glycol dimethacrylate 0.7 weight section, and the isopropyl par carbonate 0.3 weight section were mixed. This mixed liquor was poured into the glass test tube, and after nitrogen replaced the interior, it sealed. It was immersed in the warm water tub which carries out the temperature control of this test tube by the program controller, and was 6 hours and 30 degrees C at 28 degrees C, and it heated at 2 hours and 60 degrees C by 2 hours and 50 degrees C, and heated [4 hours and 32 degrees C / 3 hours and 40 degrees C] at 105 degrees C among the air furnace further by 1.5 hours and 80 degrees C for 2 hours for 2 hours, and the polymerization was performed. The round bar of the obtained copolymer was cut and the contact lens after cutting and polish was obtained.
(2) Antibacterial measurement: All operations below the number measuring method of bacilli were performed in sterile. cultivation of I and a bacillus: the following bacilli -- respectively -- a slant medium -- 37 degrees C and the 16 - 24-hour 3rd at least] generation passage -- carrying out -- 8-10ml of bouillon -- a transplant -- it cultivates for 16 to 24 hours, and let 37 degrees C be fungus liquid This bacillus was saved at 15 degrees C, and was used within three days.
RO, assay strain: Escherichia coli (Escherichia coli) and Staphylococcus aureus (Staphylococcus aureus ATCC 6538P)
HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 5.0x105 to 3.0x106. (1) It prepared by - (2), and it was immersed in the 1ml of the above-mentioned fungus liquid, and the contact lens which carried out ultraviolet-rays sterilization was saved at 37 degrees C. The culture medium of after (after [a preservation start] 0 hour and, and 18 hours) was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).
[0094] (Example 27)
(1) Composition of vinyl benzethonium: Make 2-crawl ethanol act on benzethonium chloride under boron-fluoride existence, the potassium hydroxide and the methanol were made to react continuously, and the vinyl group was combined with benzethonium chloride.
(2) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 90.8 weight section, the triethylene-glycol dimethacrylate 4 weight section, the vinyl benzethonium 5 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were

repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced.
(3) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.
[0095] (Example 28)
(1) Composition of vinyl benzalkonium: Make 2-crawl ethanol act on a benzalkonium chloride under boron-fluoride existence, the potassium hydroxide and the methanol were made to react continuously, and the vinyl group was combined with the benzene ring of a benzalkonium chloride.
(2) The polymerization of a contact lens, cutting, polish: The 2-hydroxyethyl methacrylate 92.7 weight section, the ethylene glycol dimethacrylate 2 weight section, the vinylation benzalkonium 5 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.
[0096] (Example 29)
(1) Composition of vinyl benzethonium: It carried out like the example 27.
(2) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 25 weight section, the ethylene glycol dimethacrylate 1 weight section, the vinyl benzethonium 3 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(3) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.
[0097] (Example 30)
(1) Composition of vinyl benzethonium: It carried out like the example 27.
(2) The polymerization of a contact lens, cutting, polish: The 2, 3-dihydroxy propyl methacrylate 68.95 weight section, methyl methacrylate 26 weight section, ethylene glycol dimethacrylate 1 weight section, vinyl benzethonium 4 weight section, 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide 0.05 weight section was often mixed, and deaeration of this mixture and the nitrogen purge were performed. It was dropped at the glass type which fabricated this mixture in the contact lens configuration, 80 W/cm high-pressure mercury lamp was used for this, and ultraviolet rays were irradiated for 100 seconds in 10cm of distance. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making the obtained contact lens swell in pure water and washing it.
(3) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.
[0098] (Example 31)
(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 73.7 weight section, the methyl methacrylate 25 weight section, the ethylene glycol dimethacrylate 1 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained.
(2) Plasma treatment: Next, low-temperature plasma treatment of this contact lens was carried out for 30 seconds among the air atmosphere of degree of vacuum 0.1torr within the plasma polymerizer by the electric discharge frequency of 13.56MHz, and electric discharge power 200W.
(3) Graft polymerization: It was immersed in benzalkonium-chloride solution, 60 degrees C of contact lenses which carried out plasma treatment were warmed for 1 hour, and the lens front face was made to carry out the graft polymerization of the benzalkonium chloride.
(4) Swelling and elution : elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.
(5) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.
[0099] (Example 32)
(1) Composition of vinyl benzethonium: It carried out like the example 37.

(2) The polymerization of a contact lens, cutting, polish: The methyl methacrylate 90.8 weight section, the triethylene-glycol dimethacrylate 4 weight section, the vinyl benzethonium 5 weight section, and the azobis (2,4-dimethylvaleronitrile) 0.2 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was produced. The obtained rod was ground and antibacterial resin powder was produced.

[0100] (3) Production of an antibacterial contact lens container: It often mixed, injection molding of the antibacterial powder 10 weight section produced by the polyethylene 90 weight section and (2) was carried out, and the contact lens container was produced.

(4) Antibacterial measurement: The number measuring method of bacilli. All the following operations were performed in sterile.

I, cultivation of a bacillus: It carried out by the same method as an example 26.

RO, assay strain: Escherichia coli (Escherichia coli)

HA, antibacterial evaluation: Using the nutrient broth culture medium, each bacillus was prepared so that the number of bacilli per ml might be set to 103 to 3.0x104. (1) It prepared by - (2), the 1ml of the above-mentioned fungus liquid was put into the contact lens container which carried out ultraviolet-rays sterilization, and it saved at 37 degrees C. The culture medium 18 hours after after a preservation start was measured after dilution with the sterilization buffered saline solution with the pour-plate culture method (for 37 degrees C and two days) which used the culture medium for the number measurement of bacilli (the EIKEN CHEMICAL CO., LTD. make, standard agar medium).

[0101] (Example 26 of comparison)

(1) The polymerization of a contact lens, cutting, polish: 2, the 3-dihydroxy propyl methacrylate 70.7 weight section, the methyl methacrylate 25 weight section, the ethylene glycol dimethacrylate 1 weight section, the benzethonium chloride 3 weight section, and the isopropyl par carbonate 0.3 weight section were often mixed, this mixture was put into the glass sealed tube, a nitrogen purge and deaeration were repeated and the interior was heat-sealed under the vacuum. Among warm water, it was heated at 5 hours and 50 degrees C by 10 hours and 40 degrees C, and this sealed tube was heated [30 degrees C] at 70 degrees C by 60 degrees C for 3 hours for 3 hours for 5 hours, was further heated at 100 degrees C among the air furnace for 2 hours, the polymerization was performed, and the round bar was obtained. Cutting of the obtained rod was carried out and the contact lens was obtained. Elution of an effluent was completed at the same time it was under a physiological saline and carried out water absorption of the specified quantity, after making this lens swell in pure water and washing it.

(2) Antibacterial measurement: The number measuring method of bacilli. It carried out like the example 26.

[0102] The result of the antimicrobial activity of each example and the example of comparison is shown below.

[0103]

[Table 9]

実施例 番号	残存菌数	
	大腸菌	黄色ブドウ球菌
26	< 20	< 20
27	< 20	< 20
28	< 20	< 20
29	< 20	< 20
30	< 20	< 20
31	< 20	< 20
対照26	$> 10^8$	$> 10^8$
対照27	$> 10^8$	$> 10^8$
対照28	$> 10^8$	$> 10^8$
対照29	$> 10^8$	$> 10^8$
対照30	$> 10^8$	$> 10^8$
対照31	$> 10^8$	$> 10^8$
比較26	10^6	10^6

[0104]

[Table 10]

実施例	残存菌数	
番号	大腸菌	黄色ブドウ球菌
32	＜ 20	＜ 20
対照32	＞ 10^8	＞ 10^8

[0105] A result shows the number of residual bacilli 18 hours after preservation. The contrast in examples 26-30 puts a contact lens material with the same other composition excluding an antibacterial substance. Moreover, the contrast in an example 31 puts the contact lens material which has not carried out surface treatment of the antibacterial substance. The contrast in an example 32 puts a contact lens container with the same other composition excluding an antibacterial substance.
[0106] The contact lens and contact lens container which were shown in the example were boiled, respectively, and the existence of elution was checked. Elution of an antibacterial substance was checked [container / contact lens] from neither of the contact lenses. On the other hand, elution was accepted from the contact lens shown in the example of comparison.
[0107]
[Effect of the Invention] As stated above, in this invention, a benzalkonium chloride, benzethonium chloride, etc. are combined firmly also in the complex of an antibacterial metal, chitosan and its derivative, a biguanide derivative especially chlorhexidine, an acridine and its derivative, inside or an ETAKU lysine, and quarternary ammonium salt. Therefore, it has the effect that the hardly generated contact lens which does not almost have the elution of an antibacterial substance which disinfection does not need and contact lens preservation containers, such as bacteria and mold, a contact lens preservative container, a contact lens cleaning agent container, or dissolution water a contact lens preservative, a cleaning agent and the container for disinfectants is obtained, over a long period of time.

[Translation done.]

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(71)出願人　000002369
セイコーエプソン株式会社
東京都新宿区西新宿２丁目４番１号
(72)発明者　牛山　洋一
長野県諏訪市大和３丁目３番５号セイコーエプソン株式会社内
(72)発明者　片桐　寛司
長野県諏訪市大和３丁目３番５号セイコーエプソン株式会社内
(72)発明者　宮林　利行
長野県諏訪市大和３丁目３番５号セイコーエプソン株式会社内
(74)代理人　弁理士　鈴木　喜三郎　(外１名)

最終頁に続く

(54)【発明の名称】　抗菌性樹脂成形体及びその製造方法

(57)【要約】
【目的】　本発明の目的は細菌、カビ等のほとんど発生しない、殺菌処理を必要としない、抗菌性物質の溶出の殆ど無い、コンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器を得ることにある。
【構成】　本発明は、コンタクトレンズもしくはコンタクトレンズ関連用品の容器の内部又は表面に共重合、グラフト重合、その他の方法で抗菌性有機物質を結合させること、もしくは抗菌性金属を錯体として強固に結合させることにより、その殺菌効果により細菌、カビ等のほとんど発生しない、殺菌処理を必要としないコンタクトレンズ及びコンタクトレンズ関連用品の容器を得ることを特徴とする。

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【特許請求の範囲】

【請求項１】抗菌性金属錯体を混在させたことを特徴とする抗菌性樹脂成形体。

【請求項２】抗菌性金属錯体を化学結合させたことを特徴とする抗菌性樹脂成形体。

【請求項３】抗菌性有機化合物を化学結合させたことを特徴とする抗菌性樹脂成形体。

【請求項４】混在させる抗菌性金属錯体の抗菌性を有する金属または金属イオンが銀、銅、亜鉛、ゲルマニウム、錫、ビスマスおよびコバルトからなる群より選ばれた１種または２種以上の金属または金属イオンであることを特徴とする請求項１記載の抗菌性樹脂成形体。

【請求項５】化学結合させる抗菌性金属錯体の抗菌性を有する金属または金属イオンが銀、銅、亜鉛、ゲルマニウム、錫、ビスマスおよびコバルトからなる群より選ばれた１種または２種以上の金属または金属イオンであることを特徴とする請求項２記載の抗菌性樹脂成形体。

【請求項６】抗菌性有機化合物がキトサンまたはその誘導体、クロルヘキシジンまたはその誘導体、第四級アンモニウム塩である塩化ベンザルコニウム、塩化ベンゼトニウムまたはその誘導体、アクリジンまたはその誘導体からなる群より選ばれた１種または２種以上の抗菌性有機化合物であることを特徴とする請求項３記載の抗菌性樹脂成形体。

【請求項７】請求項１～６のいずれかに記載の樹脂成形体がコンタクトレンズであることを特徴とする抗菌性樹脂成形体。

【請求項８】請求項１～６のいずれかに記載の樹脂成形体がコンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器であることを特徴とする抗菌性樹脂成形体。

【請求項９】銀、銅、亜鉛、ゲルマニウム、錫、ビスマスおよびコバルトからなる群より選ばれた１種または２種以上の抗菌性金属をアセトナト錯体として樹脂中に混在させたことを特徴とする抗菌性樹脂成形体の製造方法。

【請求項１０】銀、銅、亜鉛、ゲルマニウム、錫、ビスマスおよびコバルトからなる群より選ばれた１種または２種以上の抗菌性金属をアセトナト錯体にラジカル重合可能な不飽和二重結合を有する官能基を結合させ、それを重合性モノマーと共重合させることにより抗菌性有機化合物を樹脂に結合させることを特徴とする抗菌性樹脂成形体の製造方法。

【請求項１１】キトサンまたはその誘導体、クロルヘキシジンまたはその誘導体、第四級アンモニウム塩である塩化ベンザルコニウム、塩化ベンゼトニウムまたはその誘導体、アクリジンまたはその誘導体からなる群より選ばれた１種または２種以上の抗菌性有機化合物にラジカル重合可能な不飽和二重結合を有する官能基を結合させ、それを重合性モノマーと共重合させることにより抗菌性有機化合物を樹脂に結合させることを特徴とする抗菌性樹脂成形体の製造方法。

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【請求項１２】キトサンまたはその誘導体、クロルヘキシジンまたはその誘導体、第四級アンモニウム塩である塩化ベンザルコニウム、塩化ベンゼトニウムまたはその誘導体、アクリジンまたはその誘導体からなる群より選ばれた１種または２種以上の抗菌性有機化合物の持つ水酸基をコンタクトレンズ素材のカルボキシル基と反応させエーテル結合をつくることにより抗菌性有機化合物を樹脂に結合させることを特徴とする抗菌性樹脂成形体の製造方法。

【請求項１３】キトサンまたはその誘導体、クロルヘキシジンまたはその誘導体、第四級アンモニウム塩である塩化ベンザルコニウム、塩化ベンゼトニウムまたはその誘導体、アクリジンまたはその誘導体からなる群より選ばれた１種または２種以上の抗菌性有機化合物の持つカルボキシル基をコンタクトレンズ素材の水酸基と反応させエーテル結合をつくることにより抗菌性有機化合物を樹脂に結合させることを特徴とする抗菌性樹脂成形体の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は細菌、カビ等がほとんど発生しない抗菌性を有する樹脂成形体及びその製造方法に関し、更に言えば、細菌、カビ等がほとんど発生しない抗菌性を有する、即ち、安全かつ取り扱いの容易なコンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、及び、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器、並びに、それらの製造方法に関する。

【０００２】

【従来の技術】現在一般的に使用されているコンタクトレンズはハードコンタクトレンズとソフトコンタクトレンズに大別される。前記各コンタクトレンズはそれぞれ長所と短所を合わせ持つ。即ち、ハードコンタクトレンズは視力矯正効果が優れる等多くの利点を有している。その反面、機械的に角膜に傷を付け易く、そのため角膜感染症等の障害を受けることがある。一方、ソフトコンタクトレンズは親水性の付与により装用感が飛躍的に向上し、これまで問題であった角膜への酸素の補給の不足も含水により解決されつつある。しかし、含水性のものは菌による汚染を受け易く、それと知らずに装用を続ける結果、角膜炎、角膜潰瘍等の感染症を起こすことがしばしばある。また、それを防ぐための滅菌処理は非常に煩雑であり、ソフトコンタクトレンズがハードコンタクトレンズに比べ国内での装用率が低い一つの原因となっている。

【０００３】また、コンタクトレンズの関連用品の容器、即ち、コンタクトレンズ保存容器、コンタクトレン

ズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器についても使用時に容器中に混入した細菌、カビが繁殖して二次感染を起こすことがあり、保存剤、洗浄剤等の中に抗菌剤を加えることによりこれら微生物の繁殖を抑えている。しかし、多量な抗菌剤或は強い抗菌剤を使用することはコンタクトレンズのためにも、また、角膜のためにも好ましくなく、抗菌剤を添加せずに微生物の繁殖を抑制する方法が模索されてきた。抗菌性物質を被覆した樹脂等の開発は試みられているが抗菌物質の溶出が多く、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器には適さない。

【0004】

【発明が解決しようとする課題】ハードコンタクトレンズは一般に菌による汚染を比較的受けにくいといわれているものの、装用中に細菌やカビに感染し、そのため角膜が感染症等の障害を受けることがある。ソフトコンタクトレンズは材料自体が親水性のため、レンズの内部で細菌、カビ等の繁殖による重篤な感染症を起こし易く、また、取り扱いには注意を必要とすると同時に制菌、殺菌操作が煩雑であった。

【0005】そのため抗菌性を有するコンタクトレンズに対する要望が高まっているが、それにも拘らず以前には期待に応えられる技術は開発されていなかった。例えば、キトサン誘導体を基材として用いたコンタクトレンズ（特開昭63－217319号公報）及びキトサン誘導体を含有する樹脂被膜を形成したコンタクトレンズが（特開平3－102313号公報）提案されてはいるが光学性能並びに抗菌力の持続性（寿命）が不十分である。

【0006】本発明は上記のような問題点を解決するためになされたものである。すなわち本発明の目的とするところは細菌、カビ等の微生物による汚染がほとんど起こらないコンタクトレンズを提供することにある。

【0007】

【課題を解決するための手段】本発明のコンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器は抗菌性金属錯体または抗菌性有機化合物を化学結合または混在させることにより樹脂成形体に抗菌性を賦与したことを特徴とする。そのために抗菌性物質が満たすべき条件は以下の通りである。（1）　コンタクトレンズは直接角膜、結膜に接する上に、レンズからの溶出物は涙液と共に消化管に移行するため安全性に特に注意を払う必要がある。従ってコンタクトレンズ及びそれに関連する容器に結合させる抗菌性物質は安全性が高いこと、（2）結合によって抗菌活性が失われないこと、そのためにはレンズとの結合に関与する反応基を有し、かつ、その反応基が抗菌作用を発現する官能基と異なること、（3）レンズ素材に結合した場合本来のレンズの持つ光学性能を失わないこと、すなわち、レンズモノマーとの相溶性が良く、重合方法の選択の自由度が大きいこと、（4）レンズ素材に結合した場合本来のレンズの持つ加工性を失わないこと、（5）それらがコンタクトレンズに強固に結合し、または、補足され溶出が殆ど無いことが必要条件となる。

【0008】本発明者らが課題を解決するため、鋭意研究を重ねた結果、抗菌性金属の錯体、キトサン及びその誘導体、ビグアニド誘導体、特にクロルヘキシジン、アクリジン及びその誘導体、なかでもエタクリジン、並びに第四級アンモニウム塩、なかでも塩化ベンザルコニウム、塩化ベンゼトニウム等を上記条件を満たしたまま強固に樹脂に結合する方法を見いだし、本発明を完成するに至った。以下に上記抗菌性物質及びそれらのコンタクトレンズへの結合方法についてについて説明する。

【0009】（1）抗菌性金属錯体

従来より、ある種の金属又は金属イオンが抗菌性又は殺菌性を有することが知られている。例えば、硝酸銀は以前から消毒剤として用いられている。同様に銀、銅、鉛、錫、亜鉛、ビスマス、カドミウム、クロム、ゲルマニウム、コバルト等金属及びそれらの化合物の抗菌、殺菌性が知られている。先に述べた通りコンタクトレンズ及びそれに関連する容器に結合させる抗菌性物質は安全性が高いこと、結合が強固で溶出が殆ど無いことが必須条件となる。このような見地から少なくとも鉛、カドミウム、クロムは生体に悪影響を及ぼすことが知られており、コンタクトレンズ及びその関連容器に結合させる抗菌性物質としては好ましくない。銀、銅、錫、亜鉛、ビスマス、ゲルマニウム、コバルトは溶出が微量であれば問題ない。ゲルマニウムには保健作用があること（特公昭63－25618号公報）が知られており、ゲルマニウム結合樹脂を保健上の目的で利用することもできる。

【0010】金属またはそのイオンを結合又は保持する方法は多数ある。例えば、

1）ゼオライトの付着又は含有（特開昭62－241939号公報、特開平1－186804号公報）

2）混入、被着（特公昭63－25618号公報）

3）アルミノ珪酸塩（特公平2－46620号公報）

4）N－長鎖アシルアミノ珪酸塩（特開平3－20363号公報）

5）ハイドロキシアパタイト（特開平3－90007号公報）

等が報告されている。しかし、ハイドロキシアパタイト及びアルミノ珪酸塩はコンタクトレンズに用いるには光学性能が十分でない。また、金属自信の混入や被着では結合が弱く装用中に抗菌性金属の溶出が起こるため、強固に結合しているかまたは強固に補足されていることが

望ましい。

【0011】本発明者らが課題を解決するため、鋭意研究を重ねた結果、抗菌性金属のアセチルアセトン錯塩であるアセチルアセトナト金属錯体、あるいはベンゾイルアセトン錯塩であるベンゾイルアセトナト金属錯体が、コンタクトレンズ材料として好適な透明プラスチックを形成する多くの重合性モノマーに溶解し、重合組成物中に強固に組み込まれることを見いだした。

【0012】さらに研究を進めた結果、ベンゾイルアセトナト金属錯体のベンゼン環にラジカル重合可能な不飽和二重結合を有する官能基を付加することによって、抗菌物質がコンタクトレンズ材料の重合性モノマーと共重合しポリマー主鎖中に直接組み込まれるため、長期間の使用によっても全く溶出することがないことを見いだした。しかも、重合性モノマーに対する溶解性は十分にあり、また重合性モノマーと重合方法の選択の自由度が大きいことも確認され、本発明を完成するに至った。

【0013】（2）キトサン及びその誘導体

（a）キトサン及びその誘導体の抗菌性：　キチン誘導体、中でもキトサンは大腸菌のような有害微生物の生育をそれぞれ阻害する。フザリウム菌の生育は、培地に0．1%キトサン添加で完全に阻止され、大腸菌の増殖は0．02%キトサン濃度で阻止される（昭和60年度日本農芸化学会西日本支部大会、1985年11月12日、要旨33頁）。これらカビや細菌の増殖を阻害するキトサン濃度は微生物の種類により異なる。また、低分子キトサンは高分子キトサンより低い濃度でこれら微生物の増殖を阻止する。また、水酸基の水素を4級アンモニウム基を含む化合物に置換した多糖類も抗菌性を示すことが報告されている（特開平3－70701号公報）。

【0014】（b）キトサン誘導体のコンタクトレンズへの結合：　キチン誘導体の合成高分子への結合には様々の方法がある。例えば、それぞれ、高分子表面をカルボキシル化、キチン誘導体をジエチルアミノエチル（以下DEAEと略す）化しておき両者を結合させる方法（高分子学会講演要旨集：39（4），1303，1990）が報告されている。また、キチン、キトサン及びその誘導体をポリイソシアネート化合物を用いて高分子化合物の水酸基またはカルボキシル基に結合させる方法（特開平2－41473号公報）がある。その他、キトサン誘導体を極性有機溶媒に溶解し、成形後、ホルムアルデヒド、グルタルアルデヒドもしくはエピクロルヒドリンで処理して架橋させる方法（特公昭63－21731 9号公報）等が報告されている。本発明者らが課題を解決するため、上記反応を参考として鋭意研究を重ねた結果、キトサンまたはその誘導体が本来の機能を失うことなくコンタクトレンズ素材に結合し、しかも抗菌活性を発現する条件を見いだし、発明を完成するに至った。

【0015】（3）クロルヘキシジンは1954年イギリス、I．C．I．研究所のデイビス（Davis，G．E．）によって研究されたビスジグアニド（bisdiguanide）化合物の中で最も強力な殺菌剤で、臨床各領域で消毒剤として用いられていることが英国薬理学会誌（British J. of Pharmacology,9 ,192(1954)））に報告されている。グラム陽性及びグラム陰性菌に広く抗菌作用を表すが、グラム陰性菌よりもグラム陽性菌に対してより効果的である。緑膿菌（Psudomonas）やプロテウス（Proteus）のある種のものに対しては比較的効力が弱く、抗酸性菌、芽胞及びウィルスには無効である。in vitro試験では、四級アンモニウム系、フェノール系あるいはヨード製剤などの他の殺菌剤よりも強い殺菌効果を示す。効力は中性か弱アルカリ性で最も強く、血液・膿その他の有機物が存在すると低減される。ペニシリンサルファ剤などと拮抗性がなく、刺激性も弱く、また耐性菌を生じにくい。

【0016】クロルヘキシジンのコンタクトレンズへの結合：　クロルヘキシジンの合成高分子への結合には様々の方法がある。例えば、特公昭56－34203号公報記載のとおり、酸性基を有するビニルモノマーと共重合した樹脂で各種材料を加工し、酸性基を有する樹脂を各種材料表面に付着させた後、クロルヘキシジン塩の水溶液に接触させ、クロルヘキシジンを重合成分として含有されている樹脂中の酸性基に反応させて固定し、各種材料に抗菌性を賦与するという方法が知られている。

【0017】本発明者らはクロルヘキシジンまたはその塩が重合性ビニルモノマーとしてグリシジルメタクリレート、グリシジルアクリレートなどのカルボキシル基を持つモノマー、アクリル酸、メタクリル酸、イタコン酸などのカルボキシル基をもつモノマー、スチレンスルホン酸、2－アクリルアミド－2－メチルプロパンスルホン酸などのスルホン酸基を持つモノマー、そのほかメチルアクリレート、エチルアクリレート、エチルメタクリレートなどのエステル基を持つモノマー、無水マレイン酸、無水イタコン酸などの酸無水物等、コンタクトレンズ素材と共重合することにより、本来のコンタクトレンズのもつ光学性能、装用感を保持したまま抗菌性を有する安全なコンタクトレンズとして使用することができることを見い出した。なお、ラジカル重合可能な不飽和二重結合を有する官能基を結合させ、それを重合性モノマーと共重合またはグラフト重合することもできる。

【0018】（4）　エタクリジンは　日本薬局方に報告されている通り、1919年モーゲンノース（Morgenroth）、シュナイザー（Schnizer）らがアクリフラビンを改良して作った殺菌消毒薬である。各種化膿菌特に連鎖球菌、ウェルシュ菌、ブドウ球菌、淋菌などに対し、静菌並びに殺菌作用がある。in vitroでは連鎖球菌に対し1：120，000の希釈液でも有効であるが、生体内では1：40，000

が最小有効濃度である。生体組織に刺激を与えず、深達性で、血清たん白の存在によって作用が減弱されない特徴がある。作用機序は明確でないが、アクリジニウムイオンとなって細菌の呼吸酵素を阻害するためであるといわれ、現在、副作用の少ない殺菌消毒剤として広く用いられている。ところが抗菌性を失わせずにコンタクトレンズ等の樹脂にエタクリジン又はその誘導体を強固に結合させる方法は以前には報告がなかった。

【００１９】以下、本発明の詳細な説明をする。抗菌活性を失わせずエタクリジンを合成高分子へ結合させるにはエタクリジンのエトキシ基を樹脂の官能基と反応性のある官能基に置換することが必要であるが、活性基であるアミノ基が修飾を受けない条件を選ぶ、保護基を付ける、又は、反応後還元することにより可能である。ワグナーらの方法（Ｗａｇｎｅｒら，Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，７２，３４７７（１９５０））を応用し、エタクリジンのエトキシ基を水酸基に置換しておき、コンタクトレンズのカルボキシル基と反応させてエステル結合によりコンタクトレンズにエタクリジンを結合できる。また、フォーゲルら（Ｖｏｇｅｌ　ｅｔ　ａｌ．：Ｊ．Ｃｈｅｍ．Ｓｏｃ．，６１６（１９４８））らの反応を用いればエタクリジンのエトキシ基をハロゲンに置換しておき、水素を置換した合成高分子の水酸基と反応させ、脱水することにより、エーテル結合によりレンズにエタクリジンを結合させることができる。

【００２０】更に、グレディら（Ｇｒｅｄｙ　ｅｔ　ａｌ．：Ｂｕｌｌ．Ｓｏｃ．Ｃｈｉｍ．Ｆｒａｎｃｅ，３（５），１０９３（１９３６））、ヘニオンら（Ｈｅｎｎｉｏｎ　ｅｔ　ａｌ：Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，５６，１８０２（１９３４））またはラーロックら（Ｌａｒｏｃｋ　ｅｔ　ａｌ．：Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，１０６（１５），４２１８（１９８４））の反応を利用すればエタクリジンのエチル基の代わりにラジカル重合可能な不飽和二重結合を有する官能基、例えばビニル基、アリル基、アクリル基、メタクリル基等が付加した化合物を付加することによって、抗菌物質がコンタクトレンズ材料の重合性モノマーと共重合しポリマー主鎖中に直接組み込むことができる。

【００２１】（５）第四級アンモニウム塩

古くから安全な消毒剤として利用されてきた第四級アンモニウム塩、中でも塩化ベンザルコニウム、塩化ベンゼトニウム、有機シリコン系アンモニウム塩は抗菌性コンタクトレンズ用抗菌性有機化合物として好適な化合物である。第四級アンモニウム塩が強い抗菌性示すことは古くから知られている。中でも塩化ベンザルコニウム及び塩化ベンゼトニウムは安全性の高い強力な抗菌剤として広く用いられており、一般家庭で手、足、傷の消毒に用いられている以外に外科手術時の消毒にも用いられている。ドマック（Ｄｏｍａｇｋ）は１９３５年に第四級アンモニウム塩のある種のものに強力な殺菌力のあることを報告し、クーン（Ｋｕｈｎ）は１９４０年に更に多数の表面活性化合物について詳細な研究を行い、陰電荷を帯びる細菌に陽電荷を帯びる逆性石ケンが吸着され、菌体表面に集積し、菌体たん白を変性させると報告した。第四級アンモニウム塩の一般式が［$C_6H_5CH_2N(CH_3)_2R$］$^+Cl^-$Dでで示されるもののなかで、RがC_8H_{17}～$C_{18}H_{37}$のアルキル基のものが強い殺菌力と優れた洗浄作用を有することがわかり、本物質は塩化ベンザルコニウムとして広く用いられている。

【００２２】一方、ローリンス（Ｒａｗｌｉｎｓ）ら（J.Am.Pharm.Assoc.,32,11(1943)）及びジョスリンら（Ｊｏｓｌｙｎら、J.Am.Pharm.Assoc.,32,49(1943)）が第四級アンモニウム化合物を合成し、その殺菌力を研究し、塩化ベンゼトニウムと塩化メチルベンゼトニウムが最も強力であると報告した。現在、塩化ベンゼトニウムも安全かつ強力な抗菌剤として広く用いられている。ところが抗菌性及び光学性能を失わせずにコンタクトレンズ等の樹脂に第四級アンモニウム塩を強固に結合させる方法は以前には報告がなかった。

【００２３】第四級アンモニウム塩の合成高分子への結合方法の例をあげる。グレディらの反応（Ｇｒｅｄｙ　ｅｔ　ａｌ．：Ｂｕｌｌ．ｓｏｃ．ｃｈｉｍ．Ｆｒａｎｃｅ，３（５），１０９３（１９３６））、ヘニオンらの反応（Ｈｅｎｎｉｏｎ　ｅｔ　ａｌ：Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，５６，１８０２（１９３４））またはバックマンらの方法（Ｂａｃｈｍａｎ　ａｎｄ　Ｈｅｌｌｍａｎ，Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，７０，１７７２（１９４８））を利用すれば第四級アンモニウム塩にラジカル重合可能な不飽和二重結合を有する官能基、例えばビニル基、アリル基、アクリル基、メタクリル基等が付加した化合物を付加することによって、抗菌物質がコンタクトレンズ材料の重合性モノマーと共重合しポリマー主鎖中に直接組み込むことができる。また、皆川らの方法（皆川基：繊消費、１７、２５６（１９７６））を応用すれば有機シリコン系第四級アンモニウム塩を樹脂に固定することができる。

【００２４】上記抗菌性物質は抗菌性を付与するための必須成分であり、０．１～２０重量％含有されることが好ましい。０．１重量％未満であると抗菌効果が小さく、２０重量％を越えた場合は、重合性モノマーとの相溶性が低下するため、重合して得られるコンタクトレンズに白濁やくもりが発生し、透明性が失われるので好ましくない。

【００２５】上記の方法により長期間の使用によっても全く溶出することがない抗菌性物質の結合したコンタクトレンズが得られる。しかも、重合性モノマーに対する溶解性は十分にあり、また重合性モノマーと重合方法の選択の自由度が大きい。なお、スルファミン系抗生物質、ポリミキシン系抗生物質、マクロライド系抗生物質も同様な理由で抗菌性コンタクトレンズ用抗菌性物質と

して利用することが出来る。

【0026】本発明における重合性モノマーとは、一般的に用いられるラジカル重合可能な化合物であり、ビニル基、アリル基、アクリル基、またはメタクリル基等を分子中に1個以上含む化合物を示す。具体的には、アルキル（メタ）アクリレート、ハロゲン化アルキル（メタ）アクリレート、シロキサニルアルキル（メタ）アクリレート、フルオロ（メタ）アクリレート、ヒドロキシアルキル（メタ）アクリレート、ポリエチレングリコール（メタ）アクリレート、多価アルコールの（メタ）アクリル酸エステル、ビニル（メタ）アクリレート等の（メタ）アクリル酸エステル類、スチレンの誘導体、Ｎ－ビニルラクタム、（多価）カルボン酸ビニル等のビニル化合物、（多価）カルボン酸アリル、アリルカーボネート等のアリル化合物等が挙げられる。さらに具体的には、例えば、スチレンおよびメチルスチレン、ジメチルスチレン、クロルスチレン、ジクロルスチレン、ブロムスチレン、ｐ－クロルメチルスチレン、ジビニルベンゼン、アクリル酸、メチルアクリレート、エチルアクリレート、ｎ－ブチルアクリレート、フェニルアクリレート、フェノキシエチルアクリレート、アクリル酸テトラヒドロフルフリル、２－ヒドロキシエチルアクリレート、２－ヒドロキシプロピルアクリレート、２－アクリロイルオキシエチルコハク酸、２－アクリロイルオキシエチルフタル酸、メタクリル酸、メチルメタクリレート、エチルメタクリレート、ｎ－ブチルメタクリレート、２－エチルヘキシルメタクリレート、イソボルニルメタクリレート、ベンジルメタクリレート、フェニルメタクリレート、ジシクロペンタニルメタクリレート、ジシクロペンテニルメタクリレート、２－メタクリロイルオキシエチルコハク酸、２－ヒドロキシエチルメタクリレート、２－ヒドロキシプロピルメタクリレート、２－ヒドロキシブチルメタクリレート、フマル酸、マレイン酸、イタコン酸およびそれらのエステル類、アクリロニトリル、メタクリロニトリル、Ｎ，Ｎ－ジメチルアクリルアミド、Ｎ－ビニル－２－ピロリドン、無水マレイン酸、Ｎ－置換マレイミド等が挙げられる。

【0027】さらに、架橋密度を高めるために、エチレングリコールジアクリレート、ジエチレングリコールジアクリレート、トリエチレングリコールジアクリレート、１，６－ヘキサンジオールジアクリレート、エチレングリコールジメタクリレート、ジエチレングリコールジメタクリレート、トリエチレングリコールジメタクリレート、プロピレングリコールジメタクリレート、トリメチロールプロパントリメタクリレート、ペンタエリスリトールトリアクリレート、１，４－ブタンジオールジメタクリレート、１，６－ヘキサンジオールジメタクリレート、グリセリンジメタクリレート、ジビニルベンゼンジアリルフタレート、ジエチレングリコールビスアリルカーボネート等の多官能モノマーを用いることもできる。

【0028】これらの重合性モノマーへの抗菌性物質の溶解量は一様でなく、コンタクトレンズの場合、透明性を維持し、かつ、抗菌性能を発現する範囲で適宜抗菌性物質の添加量を決定する必要がある。これらの重合性モノマーは単独で用いられるほか、２種以上を組み合わせて使用することもできる。また、重合性モノマーと錯塩および重合開始剤とからなる混合物中には、必要に応じて熱安定化剤、酸化防止剤、染色剤、着色剤、紫外線吸収剤等を少量添加することもできる。

【0029】本発明の重合は、通常の重合開始剤の存在下、加熱あるいは紫外線などの活性エネルギー線の照射によって行われる。具体的な重合開始剤としては、ラジカル重合開始剤が望ましく、例えば、ベンゾイルパーオキサイド、ジイソプロピルパーオキシジカーボネート、ｔ－ブチルパーオキシ－２－エチルヘキサノエート、ｔ－ブチルパーオキシピバレート、ｔ－ブチルパーオキシジイソブチレート、ｔ－ブチルパーオキシイソプロピルカーボネート、ラウロイルパーオキサイド、アゾビスイソブチロニトリル、アゾビス（２，４－ジメチルバレロニトリル）等が用いられる。また、活性エネルギー線の照射の場合には、ベンゾインエーテル等の光重合開始剤や必要に応じて増感剤を用いる。これらの開始剤の使用量は、使用するモノマーに対し、０．００１～２重量パーセントが望ましい。

【0030】なお、コンタクトレンズ等の表面への過酸化物生成とグラフト重合によりコンタクトレンズ素材の表面層にのモノマーを結合することができる。これはコンタクトレンズの表面を紫外線照射、コロナ放電または低温プラズマ放電等を施し、発生するラジカルにモノマーをグラフト重合するものである。方法としては、コンタクトレンズを10^{-3}～１０ｔｏｒｒの減圧下のグロー放電でレンズをプラズマ処理後、モノマーを蒸気または液体として装置内へ導入し、直接ラジカルと反応させる方法、あるいは低温プラズマ処理後、被処理基材を装置から取り出しモノマーと反応させる方法がある。

【0031】上記抗菌性金属錯体を樹脂中に混在させる方法、並びに、抗菌性金属錯体または抗菌性有機化合物を樹脂へ結合させる方法はコンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器に限らず広く抗菌性樹脂形成体の製造に利用できる。上記以外の例として、まな板等の調理用品、及び、プラスチック製箸、茶碗等の食器、及び、おもちゃ、哺乳瓶等のベビー用品、ピアス等の装飾品、自動体温計等直接皮膚や粘膜に触れるプラスチック製品、浴槽、便器等カビ、細菌の発生し易い場所で利用されているプラスチック素材等が挙げられる。

【0032】

【作用】本発明の抗菌性金属錯体または抗菌性有機化合

物を結合した樹脂成形体すなわちコンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器、並びに、抗菌性金属錯体を混在させた上記樹脂成形体はカビや細菌等の微生物の発生を防止することにより安全性を向上し、煩雑な殺菌操作を省略することができ、抗菌剤を添加する必要もない。

【００３３】

【実施例】以下実施例により、更に詳しく説明するが、本発明は、これらに限定されるものではない。

【００３４】（実施例１）

１．抗菌性金属錯体の合成

（１）亜鉛錯体の合成

フラスコにクロロスチレン１３．８ｇと乾燥エーテル１００ｍｌを入れ、これに金属マグネシウム２．４ｇを加えると発熱をともなって反応が起こった。十分反応が完結したら、これにアセトニトリル４．１ｇを加え室温で１０時間撹拌した。反応混合物に水と少量の塩酸を加えると加水分解してビニルフェニルメチルケトンを得た。ビニルフェニルメチルケトン７．２ｇと酢酸エチル４．４ｇを乾燥エーテル１００ｍｌに溶解し、これに触媒としてナトリウムエトキシドを加え５０℃で還流すると、縮合反応を起こしてビニルベンゾイルアセトンを得た。上記の方法によって得られたビニルベンゾイルアセトン２．３ｇを５％アンモニア水溶液１００ｍｌに溶解し、該ビニルベンゾイルアセトンーアンモニア水溶液を、酢酸亜鉛１．４ｇを１００ｍｌの水に溶解した酢酸亜鉛水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとビニルベンゾイルアセトナト亜鉛が得られた。

【００３５】（２）銅錯体の合成

（１）と同様の方法でビニルベンゾイルアセトンを合成した。

上記のビニルベンゾイルアセトン２．３ｇを５％アンモニア水溶液１００ｍｌに溶解し、該ビニルベンゾイルアセトンーアンモニア水溶液を、酢酸銅１．４ｇを１００ｍｌの水に溶解した酢酸銅水溶液に撹拌しながら徐々に加え、青緑色の沈澱物を得た。この沈澱物を洗浄、乾燥するとビニルベンゾイルアセトナト銅が得られた。

【００３６】（３）銀錯体の合成

（１）と同様の方法でビニルベンゾイルアセトンを合成した。

得られたビニルベンゾイルアセトン２．３ｇを１５％アンモニア水溶液１００ｍｌに溶解し、該ビニルベンゾイルアセトンーアンモニア水溶液を、硝酸銀１ｇを１０ｍｌの水に溶解した硝酸銀水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとビニルベンゾイルアセトナト銀が得られた。

【００３７】（４）ゲルマニウム錯体の合成

（１）と同様の方法でビニルベンゾイルアセトンを合成した。

得られたビニルベンゾイルアセトン２．３ｇを１０％アンモニア水溶液１００ｍｌに溶解し、該ビニルベンゾイルアセトンーアンモニア水溶液を、酸化ゲルマニウム０．２ｇを１００ｍｌの水に溶解した酸化ゲルマニウム水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとビニルベンゾイルアセトナトゲルマニウムが得られた。

【００３８】（５）錫錯体の合成

（１）と同様の方法でビニルベンゾイルアセトンを合成した。

得られたビニルベンゾイルアセトン２．３ｇを５％アンモニア水溶液１００ｍｌに溶解し、該ビニルベンゾイルアセトンーアンモニア水溶液を、酸化錫１．４ｇを１００ｍｌの水に溶解した酸化錫水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとビニルベンゾイルアセトナト錫が得られた。

【００３９】２．コンタクトレンズの作製

（試料１）２，２，３，３，４，４，４－ヘプタフルオロブチルメタクリレート５０重量部、メチルジ（トリメチルシロキシ）シリルプロピルメタクリレート４８重量部、（１）～（５）で合成した金属錯体のいずれか１種１重量部、エチレングリコールジメタクリレート０．７重量部、イソプロピルパーカーボネイト０．３重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、２８℃で６時間、３０℃で４時間、３２℃で３時間、４０℃で２時間、５０℃で２時間、６０℃で１．５時間、８０℃で２時間、更に大気炉中１０５℃で２時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。

【００４０】（試料２）メチルメタクリレート９４．８重量部、トリエチレングリコールジメタクリレート４重量部、（１）～（５）で合成した金属錯体のいずれか１種１重量部、アゾビス（２，４－ジメチルバレロニトリル）０．２重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中３０℃で１０時間、４０℃で５時間、５０℃で５時間、６０℃で３時間、７０℃で３時間加熱し、更に大気炉中１００℃で２時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。

【００４１】（試料３）２－ヒドロキシエチルメタクリレート６９．７重量部、メチルメタクリレート２４．６重量部、エチレングリコールジメタクリレート０．４重量部、（１）～（５）で合成した金属錯体のいずれか１種５重量部、イソプロピルパーカーボネイト０．３重量部をよく混合し、この混合物をガラス製封管に入れ、内

部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中３０℃で１０時間、４０℃で５時間、５０℃で５時間、６０℃で３時間、７０℃で３時間加熱し、更に大気炉中１００℃で２時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【００４２】（試料４）２，３－ジヒドロキシプロピルメタクリレート７０．７重量部、メチルメタクリレート２７重量部、エチレングリコールジメタクリレート１重量部、（１）～（５）で合成した金属錯体のいずれか１種１重量部、イソプロピルパーカーボネイト０．３重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中３０℃で１０時間、４０℃で５時間、５０℃で５時間、６０℃で３時間、７０℃で３時間加熱し、更に大気炉中１００℃で２時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【００４３】（試料５）２，３－ジヒドロキシプロピルメタクリレート６９．９５重量部、メチルメタクリレート２６重量部、エチレングリコールジメタクリレート１重量部、（１）～（５）で合成した金属錯体のいずれか１種３重量部、２，４，６－トリメチルベンゾイルジフェニルホスフィンオキサイド０．０５重量部をよく混合し、この混合物の脱気、窒素置換を行った。この混合物をコンタクトレンズ形状に成形したガラス製型に滴下し、これに８０Ｗ／ｃｍ高圧水銀ランプを用いて距離１＊０ｃｍで１００秒間紫外線を照射した。得られたコンタクトレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【００４４】３．抗菌活性の評価

菌数測定法。以下の操作は全て無菌的に行った。

イ、菌の培養：　以下の菌を、それぞれ、斜面培地で３７℃、１６～２４時間少なくとも３代継代し、ブイヨン８～１０ｍｌに移植、３７℃、１６～２４時間培養して菌液とする。この菌は１５℃に保存し、３日以内に使用した。

ロ、検定菌：　大腸菌（Escherichia coli）

ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、１ｍｌ当りの菌数が10^3～３．０×10^4となるように調製した。紫外線滅菌した試料を上記菌液１ｍｌに浸漬し、３７℃で保存した。保存開始後１８時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（３７℃、２日間）により測定した。

【００４５】表1に（１）～（５）で合成した各抗菌性金属錯体とそれぞれ組み合わせて作製した試料１～５のコンタクトレンズの抗菌活性を上記３の方法で評価した結果を示す。また、表中において「対照」というのは、抗菌性金属錯体を含まない点を除いて他の組成は各試料と同一の組成で作製されたコンタクトレンズを示している。

【００４６】また、各試料を煮沸して溶出物質の有無を確認したが、どの試料からも抗菌性物質の溶出は確認されなかった。

【００４７】

【表１】

	試料１	試料２	試料３	試料４	試料５
亜鉛錯体	6×10^4	10^4	$<10^2$	$<10^2$	$<10^2$
銅錯体	2×10^3	$<10^2$	$<10^2$	$<10^2$	$<10^2$
銀錯体	$<10^2$	$<10^2$	$<10^2$	$<10^2$	$<10^2$
ｹﾞﾙﾏﾆｳﾑ錯体	$>10^8$	$>10^8$	2×10^4	3×10^4	6×10^4
錫錯体	5×10^4	9×10^3	$<10^2$	$<10^2$	$<10^2$
対照	$>10^8$	$>10^8$	$>10^8$	$>10^8$	$>10^8$

【００４８】（実施例２）

（１）コンタクトレンズの重合、切削、研磨：　２，２，３，３，４，４，４－ヘプタフルオロブチルメタクリレート５１重量部、メチルジ（トリメチルシロキシ）シリルプロピルメタクリレート４８重量部、エチレングリコールジメタクリレート０．７重量部、イソプロピルパーカーボネイト０．３重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、２８℃で６時間、３０℃で４時間、３２℃で３時間、４０℃で２時間、５※０℃で２時間、６０℃で１．５時間、８０℃で２時間、更に大気炉中１０５℃で２時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。

（２）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度０．１ｔｏｒｒの空気雰囲気中、放電周波数１３．５６ＭＨｚ、放電電力２００Ｗで３０秒間低温プラズマ処理した。

（３）グラフト重合：　実施例１の（３）で合成したビニルベンゾイルアセトナト銀の１０重量％アセチルアセトン溶液３ｍｌに（２）でプラズマ処理したコンタクト

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レンズを添加し、素早く脱気後密封し、35℃で5分間のグラフト重合処理を行った。

【0049】（実施例3）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート71．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。

（2）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度0．1ｔｏｒｒの空気雰囲気中、放電周波数13．56MHz、放電電力200Wで30秒間低温プラズマ処理した。

（3）グラフト重合：　実施例1の（3）で合成したビニルベンゾイルアセトナト銀の10重量%アセチルアセトン溶液3ｍｌに（2）でプラズマ処理したコンタクトレンズを添加し、素早く脱気後密封し、35℃で5分間のグラフト重合処理を行った。

（4）このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【0050】表2に実施例2及び3で作製したコンタクトレンズの抗菌活性を実施例1の3に示す方法で評価した結果を示す。また、表中において「対照」というのは、各実施例と同一組成で表面処理する前のコンタクトレンズを示している。また、各実施例のコンタクトレンズを煮沸して溶出物質の有無を確認したが、どの試料からも抗菌性物質の溶出は確認されなかった。

【0051】

【表2】

	実施例2	実施例3
銀錯体	8×10^3	2×10^4
対照	$>10^8$	$>10^8$

【0052】（実施例4）

（1）アセチルアセトナト銀の合成：　アセチルアセトン2．3gを15%アンモニア水溶液100ｍｌに溶解し、該ビニルベンゾイルアセトン－アンモニア水溶液を、硝酸銀1gを10ｍｌの水に溶解した硝酸銀水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとアセチルアセトナト銀が得られた。

（2）コンタクトレンズの作製：2－ヒドロキシエチル

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メタクリレート69．7重量部、メチルメタクリレート24．6重量部、エチレングリコールジメタクリレート0．4重量部、（1）で合成したアセチルアセトナト銀5重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工後研磨しコンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【0053】（実施例5）

（1）ベンゾイルアセトナト銀の合成：　ベンゾイルアセトン2．3gを15%アンモニア水溶液100ｍｌに溶解し、該ビニルベンゾイルアセトン－アンモニア水溶液を、硝酸銀1gを10ｍｌの水に溶解した硝酸銀水溶液に撹拌しながら徐々に加え、白色の沈澱物を得た。この沈澱物を洗浄、乾燥するとベンゾイルアセトナト銀が得られた。

（2）コンタクトレンズの作製：　2－ヒドロキシエチルメタクリレート69．7重量部、メチルメタクリレート24．6重量部、エチレングリコールジメタクリレート0．4重量部、（1）で合成したベンゾイルアセトナト銀5重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工後研磨しコンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

【0054】表3に実施例4及び5で作製したコンタクトレンズの抗菌活性を実施例1の3に示す方法で評価した結果を示す。また、表中において「対照」というのは、抗菌性金属錯体を含まない点を除いて他の組成は各実施例と同一の組成で作製されたコンタクトレンズを示している。また、各実施例のコンタクトレンズを煮沸して溶出物質の有無を確認したが、どの試料からも抗菌性物質の溶出は確認されなかった。

【0055】

【表3】

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	実施例4	実施例5
銀錯体	3×10^{5}	10^{6}
対照	$>10^{8}$	$>10^{8}$

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	実施例6
銀錯体	$<10^{2}$
対照	$>10^{8}$

【0056】（実施例6）
（1）ビニルベンゾイルアセトナト銀の合成：　実施例1の（3）と同様の方法で合成した。
（2）ビニルベンゾイルアセトナト銀の重合：　メチルメタクリレート94．8重量部、アセチルアセトナト銀5重量部、アゾビス（2，4ージメチルバレロニトリル）0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を粉砕し、抗菌性樹脂粉末を作製した。
（3）抗菌性コンタクトレンズ容器の作製：　ポリエチレン90重量部及び（2）で作製した抗菌性粉末10重量部をよく混合し、射出成形し、コンタクトレンズ容器を作製した。
（4）抗菌性の測定：　菌数測定法。以下の操作は全て無菌的に行った。
イ、菌の培養：　実施例1と同様の方法で行った。
【0057】ロ、検定菌：　大腸菌（Escherichia coli）
ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が10^{3}～3．0×10^{4}となるように調製した。（1）～（2）で調製し、紫外線滅菌したコンタクトレンズ容器に上記菌液1mlを入れ、37℃で保存した。保存開始後18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。
【0058】表4に上記（1）～（3）で作製したコンタクトレンズ容器の抗菌活性を上記（4）の方法で評価した結果を示す。また、表中において「対照」というのは、抗菌性金属錯体を含まない点を除いて他の組成は各実施例と同一の組成で作製されたコンタクトレンズ容器を示している。また、上記コンタクトレンズ容器を煮沸して溶出物質の有無を確認したが、菌性物質の溶出は確認されなかった。
【0059】
【表4】

【0060】（実施例7）
（1）コンタクトレンズの重合、切削、研磨：2，2，3，3，4，4，4－ヘプタフルオロブチルメタクリレート50重量部、メチルジ（トリメチルシロキシ）シリルプロピルメタクリレート49重量部、エチレングリコールジメタクリレート0．7重量部、イソプロピルパーカーボネイト0．3重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、28℃で6時間、30℃で4時間、32℃で3時間、40℃で2時間、50℃で2時間、60℃で1．5時間、80℃で2時間、更に大気炉中105℃で2時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。
【0061】（2）コンタクトレンズへのキトサンの結合：
1）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度0．1torrの空気雰囲気中、放電周波数13．56MHz、放電電力200Wで30秒間低温プラズマ処理した。
2）グラフト重合：　プラズマ処理したコンタクトレンズをアクリル酸に浸漬し、60℃、1時間加温し、レンズ表面にアクリル酸をグラフト重合させた。
3）コンタクトレンズへのキトサンの結合：　アクリル酸をグラフト重合したコンタクトレンズをカルボジイミド水溶液に浸漬し、反応させた。次に、キチンに硫酸存在下でジエチルアミノエチルアルコールを反応させて合成したDEAE－キチンを加え、キチンを共有結合により固定化した。2M酢酸緩衝液（pH4）を用いて洗浄後、40%水酸化ナトリウムで脱アセチル化し、キトサンの結合したコンタクトレンズを得た。
（3）抗菌性の測定：　菌数測定法
以下の操作は全て無菌的に行った。
イ、菌の培養：　以下の菌を、それぞれ、斜面培地で37℃、16～24時間少なくとも3代継代し、ブイヨン8～10mlに移植、37℃、16～24時間培養して菌液とする。この菌は15℃に保存し、3日以内に使用した。
ロ、検定菌：　大腸菌（Escherichia coli）及び黄色ブドウ球菌（Staphylococcus aureus ATCC 6538P）
ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が5．0×10^{5}～3．0×10^{6}となるように調製した。（1）～（2）で調製

し、紫外線滅菌したコンタクトレンズを上記菌液1mlに浸漬し、37℃で保存した。保存開始後0時間及び18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。

【0062】（実施例8）

（1）コンタクトレンズの重合、切削、研磨：　メチルメタクリレート95．7重量部、トリエチレングリコールジメタクリレート4重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。

（2）コンタクトレンズへのキトサンの結合：　5%酢酸の水溶液に対し、1%キトサン酢酸塩溶液を調製し、この中に作製したコンタクトレンズを浸漬した。これを乾燥した後、ポリイソシアネート及びポリエチレングリコール中でコンタクトレンズにキトサンを結合させた。

（3）抗菌性の測定：　実施例7と同様の方法を用いた。

【0063】（実施例9）

（1）コンタクトレンズの重合、切削、研磨：　2－ヒドロキシエチルメタクリレート97．7重量部、エチレングリコールジメタクリレート2重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）コンタクトレンズへのキトサンの結合：　作製したコンタクトレンズをキトサンのN－メチルピロリドン溶液に浸漬後、水酸化ナトリウムで処理し、ジメチルホルムアミドで処理して架橋させた。

（3）抗菌性の測定：　実施例7と同様の方法を用いた。

【0064】（実施例10）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート71．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）コンタクトレンズへのキトサンの結合：　実施例7と同様の方法を用いた。

（3）抗菌性の測定：　実施例7と同様の方法を用いた。

【0065】（実施例11）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート69．95重量部、メチルメタクリレート26重量部、エチレングリコールジメタクリレート1重量部、トリスベンゾイルアセトナトネオジム3重量部、2，4，6－トリメチルベンゾイルジフェニルホスフィンオキサイド0．05重量部をよく混合し、この混合物の脱気、窒素置換を行った。この混合物をコンタクトレンズ形状に成形したガラス製型に滴下し、これに80W／cm高圧水銀ランプを用いて距離10cmで100秒間紫外線を照射した。得られたコンタクトレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）コンタクトレンズへのキトサンの結合：　実施例7と同様の方法を用いた。

（3）抗菌性の測定：　実施例17と同様の方法を用いた。

【0066】以下に各実施例に於ける抗菌活性の結果を示す。

【0067】

【表5】

実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
7	2.0×10^{4}	4.1×10^{4}
8	1.0×10^{4}	5.1×10^{3}
9	＜20	＜20
10	＜20	＜20
11	＜20	＜20

【0068】結果は保存18時間後の残存菌数を示す。

【0069】（実施例12）

（1）コンタクトレンズの重合、切削、研磨：　2，2，3，3，4，4，4－ヘプタフルオロブチルメタクリレート50重量部、メチルジ（トリメチルシロキシ）シリルプロピルメタクリレート49重量部、エチレングリコールジメタクリレート0．7重量部、イソプロピルパーカーボネイト0．3重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置

換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、28℃で6時間、30℃で4時間、32℃で3時間、40℃で2時間、50℃で2時間、60℃で1．5時間、80℃で2時間、更に大気炉中105℃で2時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。

（2）コンタクトレンズへのクロルヘキシジンの結合：

1）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度0．1torrの空気雰囲気中、放電周波数13．56MHz、放電電力200Wで30秒間低温プラズマ処理した。

2）グラフト重合：　プラズマ処理したコンタクトレンズをクロルヘキシジン水溶液に浸漬し、60℃1時間加温し、レンズ表面にクロルヘキシジンをグラフト重合させた。

【0070】（3）抗菌性の測定：　菌数測定法

以下の操作は全て無菌的に行った。

イ、菌の培養：　以下の菌を、それぞれ、斜面培地で37℃、16～24時間少なくとも3代継代し、ブイヨン8～10mlに移植、37℃、16～24時間培養して菌液とする。この菌は15℃に保存し、3日以内に使用した。

ロ、検定菌：　大腸菌（Escherichia coli）及び黄色ブドウ球菌（Staphylococcus aureus ATCC 6538P）

ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が5．0×10^5～3．0×10^6となるように調製した。（1）～（2）で調製し、紫外線滅菌したコンタクトレンズを上記菌液1mlに浸漬し、37℃で保存した。保存開始後0時間及び18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。

【0071】（実施例13）

（1）コンタクトレンズの重合、切削、研磨：　メチルメタクリレート96重量部、トリエチレングリコールジメタクリレート4重量部、アゾビス（2，4－ジメチルバレロニトリル）0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。

（2）コンタクトレンズへのクロルヘキシジンの結合：　実施例12と同様の方法を用いた。

（3）抗菌性の測定：　実施例12と同様の方法を用いた。

【0072】（実施例14）

（1）コンタクトレンズの重合、切削、研磨：　2－ヒドロキシエチルメタクリレート96．7重量部、エチレングリコールジメタクリレート2重量部、クロルヘキシジン1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）抗菌性の測定：　実施例12と同様の方法を用いた。

【0073】（実施例15）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、クロルヘキシジン1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）抗菌性の測定：　実施例12と同様の方法を用いた。

【0074】（実施例16）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート68．95重量部、メチルメタクリレート26重量部、エチレングリコールジメタクリレート1重量部、トリスベンゾイルアセトナトネオジム3重量部、クロルヘキシジン1重量部、2，4，6－トリメチルベンゾイルジフェニルホスフィンオキサイド0．05重量部をよく混合し、この混合物の脱気、窒素置換を行った。この混合物をコンタクトレンズ形状に成形したガラス製型に滴下し、これに80W／cm高圧水銀ランプを用いて距離10cmで100秒間紫外線を照射した。得られたコンタクトレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）抗菌性の測定：　実施例12と同様の方法を用いた。

【0075】（実施例17）

（1）ビニルクロルヘキシジンの合成：　クロルヘキシ

ジンにナトリウムアミド存在下でジメチル硫酸を作用させビニルクロルヘキシジンを合成した。

（2）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、ビニルクロルヘキシジン1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例12と同様の方法を用いた。

【0076】以下に各実施例の抗菌活性の結果を示す。又、表中において、「対照」というのは、実施例12及び13においては表面処理してないコンタクトレンズを示し、実施例14～17においては抗菌性物質を含まない点を除いて他の組成は各実施例と同一のコンタクトレンズを示している。

【0077】

【表6】

実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
12	＜ 20	＜ 20
13	＜ 20	＜ 20
14	＜ 20	＜ 20
15	＜ 20	＜ 20
16	＜ 20	＜ 20
17	＜ 20	＜ 20
対照12	＞ 10^8	＞ 10^8
対照13	＞ 10^8	＞ 10^8
対照14	＞ 10^8	＞ 10^8
対照15	＞ 10^8	＞ 10^8
対照16	＞ 10^8	＞ 10^8
対照17	＞ 10^8	＞ 10^8

【0078】結果は保存18時間後の残存菌数を示す。

【0079】（実施例18）

（1）コンタクトレンズの重合、切削、研磨：　2，2，3，3，4，4，4－ヘプタフルオロブチルメタクリレート50重量部、メチルジ（トリメチルシロキシ）シリルプロピルメタクリレート49重量部、エチレングリコールジメタクリレート0．7重量部、t－ブチルパーオキシネオデカネート0．3重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、28℃で6時間、30℃で4時間、32℃で3時間、40℃で2時間、50℃で2時間、60℃で1．5時間、80℃で2時間、更に大気炉中105℃で2時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。

（2）コンタクトレンズへのエタクリジンの結合：

1）エタクリジンの脱エチル化：　エタクリジンにヨウ化水素を作用させ、エトキシ基を水酸基に置換した。

2）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度0．1torrの空気雰囲気中、放電周波数13．56MHz、放電電力200Wで30秒間低温プラズマ処理した。

3）コンタクトレンズへのエタクリジンの結合：　上記活性化コンタクトレンズを脱エチルエタクリジンに浸漬し、60℃、1時間加温し、エタクリジンの結合したコンタクトレンズを得た。

【0080】（3）抗菌性の評価：　菌数測定法

以下の操作は全て無菌的に行った。

イ、菌の培養：　以下の菌を、それぞれ、斜面培地で37℃、16～24時間少なくとも3代継代し、ブイヨン8～10mlに移植、37℃、16～24時間培養して菌液とする。この菌は15℃に保存し、3日以内に使用した。

ロ、検定菌：　大腸菌（Escherichia coli）及び黄色ブドウ球菌（Staphylococcus aureus ATCC 6538P）

ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が5．0×10^3～3．0×10^6となるように調製した。（1）～（2）で調製し、紫外線滅菌したコンタクトレンズを上記菌液1mlに浸漬し、37℃で保存した。保存開始後0時間及び18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。

【0081】（実施例19）

（1）コンタクトレンズの重合、切削、研磨：　メチルメタクリレート96重量部、トリエチレングリコールジメタクリレート4重量部、アゾビス（2，4－ジメチルバレロニトリル）0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。

（2）コンタクトレンズへのエタクリジンの結合：　エタクリジンにヨウ化水素を作用させ、エトキシ基を水酸基に置換した。次に臭化水素により水酸基を臭素原子に置換し2－ハイドロキシ－6，9－アクリジンジアミン

を得た。一方、コンタクトレンズ基材に金属ナトリウムを反応させ水酸基の水素をナトリウムに置換し、活性化したコンタクトレンズを得た。2－ハイドロキシー6，9－アクリジンジアミンを活性化コンタクトレンズと反応させることによりエーテル結合によりレンズにを結合させた。最後に酸化された2つのアミノ基を氷酢酸中、塩化第一スズと塩酸で還元してエタクリジンを結合させたコンタクトレンズを得た。

（3）抗菌性の評価：　実施例18と同様の方法を用いた。

【0082】（実施例20）

（1）6，9－ジアミノ－2－アクリジノキシエチレン（2－ビニロキシー6，9－アクリジンジアミン　）の合成：

1）エタクリジンにヨウ化水素を作用させ、2－ヒドロキシー6，9－アクリジンジアミンとした。

2）これにエチレンカーボネイトを作用させβ－ヒドロキシエチル　6，9－ジアミノ－2－アクリジニル　エーテルとした。

3）硫酸存在下で脱水し、6，9－ジアミノ－2－アクリジノキシエチレンを合成した。

（2）コンタクトレンズの重合、切削、研磨：　2－ヒドロキシエチルメタクリレート97重量部、エチレングリコールジメタクリレート2重量部、エタクリジン1重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例18と同様の方法を用いた。但し、滅菌は高圧蒸気滅菌法を用いた。

【0083】（実施例21）

（1）6，9－ジアミノ－2－アクリジノキシエチレンの合成：

1）エタクリジンにヨウ化水素を作用させ、2－ヒドロキシー6，9－アクリジンジアミンとした。

2）これにナトリウムアミド存在下でジメチル硫酸を作用させ6，9－ジアミノ－2－アクリジノキシエチレンを合成した。

（2）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、6，9－ジアミノ－2－アクリジノキシエチレン1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例28と同様の方法を用いた。

【0084】（実施例22）

（1）6，9－ジアミノ－2－アクリジノキシエチレンの合成：

1）エタクリジンにヨウ化水素を作用させ、2－ヒドロキシー6，9－アクリジンジアミンとした。

2）これにアセチレンガスを作用させ6，9－ジアミノ－2－アクリジノキシエチレンを合成した。

（2）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート68．95重量部、メチルメタクリレート29重量部、エチレングリコールジメタクリレート1重量部、6，9－ジアミノ－2－アクリジノキシエチレン1重量部、2，4，6－トリメチルベンゾイルジフェニルホスフィンオキサイド0．05重量部をよく混合し、この混合物の脱気、窒素置換を行った。この混合物をコンタクトレンズ形状に成形したガラス製型に滴下し、これに80W／cm高圧水銀ランプを用いて距離10cmで100秒間紫外線を照射した。得られたコンタクトレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例30と同様の方法を用いた。

【0085】（実施例23）

（1）6，9－ジアミノ－2－アクリジノキシエチレンの合成：　実施例21と同様の方法で行った。

（2）コンタクトレンズの重合、切削、研磨：　メチルメタクリレート4重量部、エチレングリコールジメタクリレート1重量部、2－ヒドロキシエチルメタクリレート83．7重量部、N，N－ジメチルアクリルアミド10重量部、6，9－ジアミノ－2－アクリジノキシエチレン1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例18と同様の方法を用いた。

【0086】（実施例24）

（1）6，9－ジアミノ－2－アクリジノキシエチレンの合成：　実施例21と同様の方法で合成した。

（2）6，9－ジアミノ－2－アクリジノキシエチレンの重合：　メチルメタクリレート94．8重量部、6，9－ジアミノ－2－アクリジノキシエチレン5重量部、アゾビス（2，4－ジメチルバレロニトリル）0．2重量部をよく混合し、この混合物をコンタクトレンズ容器の金型に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この金型を70℃で1時間加熱し、更に大気炉中100℃で1時間加熱して重合を行ない、コンタクトレンズ容器を得た。

（3）抗菌性の測定：　菌数測定法。以下の操作は全て無菌的に行った。

イ、菌の培養：　実施例18と同様の方法で行った。

ロ、検定菌：　大腸菌（Escherichia coli）

ハ、抗菌性の評価：　菌を普通ブイヨン培地を用い、1ml当りの菌数が10^3～3．0×10^4となるように調製した。（1）～（2）で調製し、紫外線滅菌したコンタクトレンズ容器に上記菌液1mlを入れ、37℃で保存した。保存開始後18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。

【0087】（実施例25）

（1）6，9－ジアミノ－2－アクリジノキシエチレンの合成：実施例20と同様に行った。

（2）6，9－ジアミノ－2－アクリジノキシエチレンの重合：　メチルメタクリレート94．8重量部、6，9－ジアミノ－2－アクリジノキシエチレン5重量部、アゾビス（2，4－ジメチルバレロニトリル）0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中70℃で1時間加熱し、更に大気炉中100℃で1時間加熱して重合を行ない、丸棒を得た。得られた棒を粉砕し、抗菌性樹脂粉末を作製した。

（3）抗菌性コンタクトレンズ容器の作製：　ポリエチレン90重量部及び（2）で作製した抗菌性粉末10重量部をよく混合し、射出成形し、コンタクトレンズ容器を作製した。

（4）抗菌性の測定：　実施例24と同様の方法で行った。

【0088】（比較例18）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート27重量部、エチレングリコールジメタクリレート1重量部、エタクリジン1重量

部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の評価：　実施例18と同様の方法を用いた。

【0089】以下に各実施例及び比較例の抗菌活性の結果を示す。

【0090】

【表7】

実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
18	≦20	＜20
19	≦20	20
20	≦20	≦20
21	≦20	≦20
22	≦20	≦20
23	＜20	＜20
比較例18	＞10^8	＞10^8

【0091】

【表8】

実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
24	≦ 20	≦ 20
25	＜ 20	＜ 20
対照24	≧ 10^8	≧ 10^8
対照25	≧ 10^8	≧ 10^8

【0092】結果は保存18時間後の残存菌数を示す。また、実施例24～25に於ける対照とは、抗菌性物質を含まずその他の組成は同一のコンタクトレンズ容器をさす。各実施例に示したコンタクトレンズおよびコンタクトレンズ容器をそれぞれ煮沸して溶出の有無を確認した。いずれのコンタクトレンズからもコンタクトレンズ容器からも抗菌性物質の溶出は確認されなかった。一方、比較例に示したコンタクトレンズからは溶出が認められた。

【0093】（実施例26）

（1）コンタクトレンズの重合、切削、研磨：2，2，3，3，4，4，4－ヘプタフルオロブチルメタクリレート50重量部、トリメチル［2－［トリエトキシシリ

ル]プロピル]アンモニウム塩5重量部、メチルジ(トリメチルシロキシ)シリルプロピルメタクリレート44重量部、エチレングリコールジメタクリレート0．7重量部、イソプロピルパーカーボネイト0．3重量部を室温でよく混合した。この混合液をガラス製試験管に注入し、内部を窒素で置換した後密封した。この試験管をプログラムコントローラーで温度制御する温水槽に浸漬し、28℃で6時間、30℃で4時間、32℃で3時間、40℃で2時間、50℃で2時間、60℃で1．5時間、80℃で2時間、更に大気炉中105℃で2時間加熱し、重合を行った。得られた共重合体の丸棒を切断し、切削、研磨後コンタクトレンズを得た。

(2)抗菌性の測定：　菌数測定法

以下の操作は全て無菌的に行った。

イ、菌の培養：　以下の菌を、それぞれ、斜面培地で37℃、16～24時間少なくとも3代継代し、ブイヨン8～10ml に移植、37℃、16～24時間培養して菌液とする。この菌は15℃に保存し、3日以内に使用した。

ロ、検定菌：　大腸菌(Escherichia coli)及び黄色ブドウ球菌(Staphylococcus aureus ATCC 6538P)

ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が5．0×10^5～3．0×10^6となるように調製した。(1)～(2)で調製し、紫外線滅菌したコンタクトレンズを上記菌液1mlに浸漬し、37℃で保存した。保存開始後0時間及び18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地(栄研化学社製、標準寒天培地)を使用した混釈平板培養法(37℃、2日間)により測定した。

【0094】(実施例27)

(1)ビニルベンゼトニウムの合成：　塩化ベンゼトニウムにフッ化ホウ素存在下で2－クロルエタノールを作用させ、続いて水酸化カリウムとメタノールを反応させて塩化ベンゼトニウムにビニル基を結合させた。

(2)コンタクトレンズの重合、切削、研磨：　メチルメタクリレート90．8重量部、トリエチレングリコールジメタクリレート4重量部、ビニルベンゼトニウム5重量部、アゾビス(2，4－ジメチルバレロニトリル)0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。

(3)抗菌性の測定：　菌数測定法。　実施例26と同様に行った。

【0095】(実施例28)

(1)ビニルベンザルコニウムの合成：　塩化ベンザルコニウムにフッ化ホウ素存在下で2－クロルエタノールを作用させ、続いて水酸化カリウムとメタノールを反応させて塩化ベンザルコニウムのベンゼン環にビニル基を結合させた。

(2)コンタクトレンズの重合、切削、研磨：　2－ヒドロキシエチルメタクリレート92．7重量部、エチレングリコールジメタクリレート2重量部、ビニル化ベンザルコニウム5重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

(3)抗菌性の測定：　菌数測定法。実施例26と同様に行った。

【0096】(実施例29)

(1)ビニルベンゼトニウムの合成：　実施例27と同様に行った。

(2)コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート25重量部、エチレングリコールジメタクリレート1重量部、ビニルベンゼトニウム3重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

(3)抗菌性の測定：　菌数測定法。実施例26と同様に行った。

【0097】(実施例30)

(1)ビニルベンゼトニウムの合成：　実施例27と同様に行った。

(2)コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート68．95重量部、メチルメタクリレート26重量部、エチレングリコールジメタクリレート1重量部、ビニルベンゼトニウム4重量部、2，4，6－トリメチルベンゾイルジフェニルホスフィンオキサイド0．05重量部をよく混合し、この混合物の脱気、窒素置換を行った。この混合物をコンタクトレンズ形状に成形したガラス製型に滴下し、これに80W／cm高圧水銀ランプを用いて距離10cmで100秒間紫外線を照射した。得られたコンタクトレ

ンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（3）抗菌性の測定：　菌数測定法。実施例26と同様に行った。

【0098】（実施例31）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート73．7重量部、メチルメタクリレート25重量部、エチレングリコールジメタクリレート1重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。

（2）プラズマ処理：　次にこのコンタクトレンズを、プラズマ重合装置内で、真空度0．1torrの空気雰囲気中、放電周波数13．56MHz、放電電力200Wで30秒間低温プラズマ処理した。

（3）グラフト重合：　プラズマ処理したコンタクトレンズを塩化ベンザルコニウム水溶液に浸漬し、60℃1時間加温し、レンズ表面に塩化ベンザルコニウムをグラフト重合させた。

（4）膨潤及び溶出：このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（5）抗菌性の測定：　菌数測定法。実施例26と同様に行った。

【0099】（実施例32）

（1）ビニルベンゼトニウムの合成：　実施例37と同様に行った。

（2）コンタクトレンズの重合、切削、研磨：　メチルメタクリレート90．8重量部、トリエチレングリコールジメタクリレート4重量部、ビニルベンゼトニウム5重量部、アゾビス（2，4－ジメチルバレロニトリル）0．2重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを作製した。得られた棒を粉砕し、抗菌性樹脂粉末を作製した。

【0100】（3）抗菌性コンタクトレンズ容器の作製：　ポリエチレン90重量部及び（2）で作製した抗菌性粉末10重量部をよく混合し、射出成形し、コンタクトレンズ容器を作製した。

（4）抗菌性の測定：　菌数測定法。以下の操作は全て無菌的に行った。

イ、菌の培養：　実施例26と同様の方法で行った。

ロ、検定菌：　大腸菌（Escherichia coli）

ハ、抗菌性の評価：　それぞれの菌を普通ブイヨン培地を用い、1ml当りの菌数が10^3～3．0×10^4となるように調製した。（1）～（2）で調製し、紫外線滅菌したコンタクトレンズ容器に上記菌液1mlを入れ、37℃で保存した。保存開始後18時間後の培養液を滅菌緩衝生理食塩水で希釈後、菌数測定用培地（栄研化学社製、標準寒天培地）を使用した混釈平板培養法（37℃、2日間）により測定した。

【0101】（比較例26）

（1）コンタクトレンズの重合、切削、研磨：　2，3－ジヒドロキシプロピルメタクリレート70．7重量部、メチルメタクリレート25重量部、エチレングリコールジメタクリレート1重量部、塩化ベンゼトニウム3重量部、イソプロピルパーカーボネイト0．3重量部をよく混合し、この混合物をガラス製封管に入れ、内部を窒素置換、脱気を繰り返し、真空下溶封した。この封管を、温水中30℃で10時間、40℃で5時間、50℃で5時間、60℃で3時間、70℃で3時間加熱し、更に大気炉中100℃で2時間加熱して重合を行ない、丸棒を得た。得られた棒を切削加工し、コンタクトレンズを得た。このレンズを純水中で膨潤させ、洗浄した後、生理食塩水に浸漬して、所定量の吸水をさせると同時に、溶出物の溶出を完結させた。

（2）抗菌性の測定：　菌数測定法。実施例26と同様に行った。

【0102】以下に各実施例及び比較例の抗菌活性の結果を示す。

【0103】

【表9】

実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
26	＜20	＜20
27	＜20	＜20
28	＜20	＜20
29	＜20	＜20
30	＜20	＜20
31	＜20	＜20
対照26	＞10^8	＞10^8
対照27	＞10^8	＞10^8
対照28	＞10^8	＞10^8
対照29	＞10^8	＞10^8
対照30	＞10^8	＞10^8
対照31	＞10^8	＞10^8
比較26	10^6	10^6

【0104】

【表10】

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実施例番号	残存菌数	
	大腸菌	黄色ブドウ球菌
32	＜ 20	＜ 20
対照32	＞ 10^8	＞ 10^8

【0105】結果は保存18時間後の残存菌数を示す。実施例26～30に於ける対照とは抗菌性物質を含まず、その他の組成は同一のコンタクトレンズ素材をさす。また、実施例31に於ける対照とは抗菌性物質を表面処理していないコンタクトレンズ素材をさす。実施例32に於ける対照とは抗菌性物質を含まず、その他の組成は同一のコンタクトレンズ容器をさす。

【0106】実施例に示したコンタクトレンズおよびコンタクトレンズ容器をそれぞれ煮沸して溶出の有無を確認した。いずれのコンタクトレンズからもコンタクトレンズ容器からも抗菌性物質の溶出は確認されなかった。一方、比較例に示したコンタクトレンズからは溶出が認められた。

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【0107】

【発明の効果】以上述べたように、本発明は抗菌性金属の錯体、キトサン及びその誘導体、ビグアニド誘導体、特にクロルヘキシジン、アクリジン及びその誘導体、なかでもエタクリジン、並びに第四級アンモニウム塩、なかでも塩化ベンザルコニウム、塩化ベンゼトニウム等を強固に結合させることにより長期にわたり細菌、カビ等の殆ど発生しない、消毒のいらない、抗菌性物質の溶出の殆ど無いコンタクトレンズ、コンタクトレンズ保存容器、コンタクトレンズ保存剤容器、コンタクトレンズ洗浄剤容器、又は、コンタクトレンズ保存剤・洗浄剤・消毒剤用溶解水容器が得られるという効果を有する。

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(72)発明者　児島　忠雄
長野県諏訪市大和3丁目3番5号セイコーエプソン株式会社内
(72)発明者　最上　隆夫
長野県諏訪市大和3丁目3番5号セイコーエプソン株式会社内